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A Binary Power Generation and Salt Water Distillation Cycle

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A BINARY POWER GENERATION AND SALT WATER DISTILLATION CYCLE

BY

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ABSTRACT

This research report discusses a binary power generation and salt water distillation cycle that was the subject of a feasibility study at Florida Technological University. The thermodynamic equations are derived and the results of a parametric study to determine optimum fluid properties is presented.

This cycle produces power at efficiencies significantly higher than that of conventional cycles and at the same time produces a significant amount of fresh water. The efficiency is maintained even at the high turbine outlet temperature necessary to produce fresh water.

The important quantities in considering the cycle efficiency and the fresh water production are the heat of reaction and the absorption capacity. Changes in these quantities will have the greatest effect on the efficiency and the fresh water production.

The results of the calculations and the parametric study are presented which compare the turbine outlet temperature with the efficiency and fresh water production for a con-

ventional cycle and the binary cycle discussed here.

Conclusions are presented that this cycle should be afforded more study by means of a model plant and experimentation to validate the results calculated.

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c_p	Specific Heat
e	Energy of a system
g_c	Gravitational constant
h	Specific Enthalpy
hor	Heat of reaction
$\dot{m}$	Mass flow rate
$\dot{m}_{car}$	Mass flow rate of the carrier fluid
$\dot{m}_{CO2}$	Mass flow rate of the carbon dioxide
$\dot{m}_{H2O}$	Mass flow rate of the steam
$\dot{m}_{mix}$	Mass flow rate of the carrier fluid-CO_2 mixture
M	Fresh water produced
P	Pressure
Q	Heat release
Q_a	Heat added to the vapor
Q_{abs}	Heat release from the absorber
Q_{added}	Heat added to a system
Q_{cond}	Heat released from the condenser
Q_{cool}	Heat released from the carbonate cooler
Q_l	Heat lost by the brine
Q_r	Heat added to the boiler in the desalting plant
Q_{rs}	Heat added to the regenerator-superheater

R	Ratio of pounds of carrier fluid to pounds of CO_2 absorbed
IR	Gas Constant
T	Temperature
T_{1s}	Isentropic turbine inlet temperature
u	Internal energy
~~v~~	Velocity
v	Specific volume
v_{car}	Specific volume of the carrier fluid
v_{mix}	Specific volume of the carrier fluid-CO_2 mixture
W	Work
W_{net}	Net work achieved from a cycle
w_p	Work of the pump per unit mass
W_p	Work of the pump per unit time
w_{pw}	Work of the Pelton wheel per unit mass
W_{pw}	Work of the Pelton wheel per unit time
w_t	Work of the turbine per unit mass
W_t	Power generated by the turbine
W_{tot}	Total power required by the pump-Pelton wheel combination
w_{ts}	Isentropic work of the turbine
z	Height above a datum
λ	Latent heat of vaporization for sea water

η	Efficiency
η_{Carnot}	Carnot cycle efficiency
η_{CO2}	CO_2 cycle efficiency
η_p	Efficiency of the pump
η_{pw}	Efficiency of the pelton wheel
η_r	Rankine cycle efficiency
η_t	Efficiency of the turbine
ω	Sea water circulation

CHAPTER 1

INTRODUCTION

The increasing demand for electricity and the increasing number of electrical products and equipment coupled with the current energy crisis and decreasing supply of fossil fuels, necessitates the most efficient means of electrical power production that man can devise to conserve energy. In 1965, electrical power generation accounted for 18.3% of the fossil fuel use[1]. At the current rate of increase, this can be expected to be approaching 25% by the year 1980. Since electrical power generation demands a large percentage of the fossil fuel supply it is evident that an increase in the efficiency of electrical power plants would save a substantial amount of the remaining fossil fuel reserves.

For example, currently the average efficiency for an electrical power generating plant is about 30%[2]. In 1970, the total amount of electrical power consumed in the United States was approximately 1.5×10^{12} kwhr or 5×10^{15} BTU[3]. At an average efficiency of 30% this amounts to 16.7×10^{15}

BTU of energy that must be supplied as fuel. If the average efficiency could be increased by 5%, 5.8×10^{15} BTU or 1.7×10^{12} kwhr of electrical energy could be produced from the same amount of fuel. On a continuous basis, the extra power generated is enough to supply the needs of 200 million average size homes.

With the depletion of the fossil fuel supply being estimated to occur within the next couple of centuries, and before the year 2000 by pessimistic sources, maximum efficiency for power generation plants is very desirable. The efficiency of the Rankine cycle, which has been the workhorse of electrical power generation, has continually increased with the addition of reheat, regeneration and other efficiency improving methods and with improvements in the basic four components of the cycle, i.e. the boiler, turbine-generator, condenser and the pump. Modern Rankine cycles have efficiencies of around 40%. It is doubtful, however, that any further significant increase in the efficiency of the cycle can be achieved.

The binary power generation and salt water distillation cycle presented in this report, operates at a higher efficiency than that of conventional cycles and at the

same time makes use of the waste heat for production of fresh water. The cycle uses CO_2, instead of steam, as the working fluid and henceforth, for brevity, it will be called the CO_2 cycle. The condenser is replaced with an absorber and the boiler with a regenerator-superheater. A full process description is given in Chapter 2.

CHAPTER 2

CO_2 ABSORPTION POWER GENERATION CYCLE

The CO_2 cycle is shown in Figure 2.1. The cycle is based on a CO_2 absorption-regeneration process conventionally used for removing CO_2 from gas streams, combined with a conventional turbine-generator for producing electricity. An absorber replaces the condenser in the Rankine cycle while a regenerator-superheater replaces the boiler. A Pelton wheel and a carbonate cooler are also added to the cycle. An overall description of the process is given in the following paragraphs.

Pictorially referring to Figure 2.1, CO_2 leaves the turbine and enters the absorber. The CO_2 at this point is at a relatively low temperature and pressure (typically 200^{o}F and 25 psia). The CO_2 is absorbed by the carrier fluid in the absorber by means of an exothermic reaction giving off an amount of heat equal to the heat of reaction of the two compounds. This heat is used in the binary cycle to heat sea water for desalination.

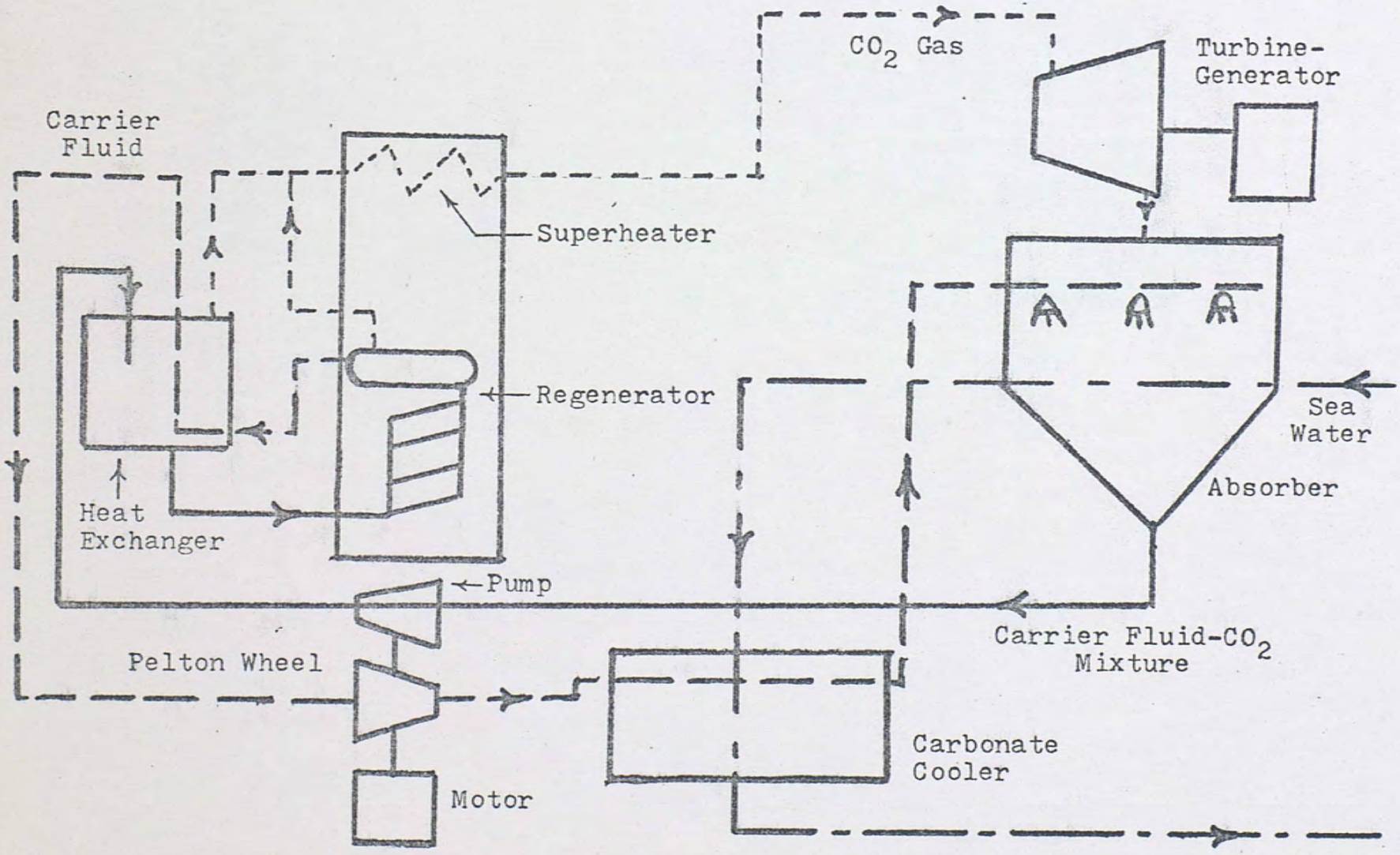

FIGURE 2.1 - CO_2 Absorption Power Generation Cycle

The CO_2-carrier fluid mixture flows to the pump where the pressure is raised to the value desired for entrance to the turbine. Constant pressure is assumed across the regenerator-superheater and the necessary turbine inlet pressure must be realized by the pump.

From the pump, the mixture proceeds to a heat exchanger where the regeneration process is initiated. In the heat exchange the mixture picks up heat from regenerated carrier fluid returning to the absorber, causing some of the CO_2 to be released. The mixture then flows to the regenerator where the bulk of the CO_2 is boiled off. The CO_2 from the regenerator is joined with the CO_2 released in the heat exchanger and is piped to the superheater where the temperature is raised to the desired value for entrance to the turbine. The CO_2 is then expanded through the turbine to power a generator to generate electricity.

The regenerated carrier fluid, meanwhile, leaves the regenerator and goes through the heat exchanger giving up heat as described previously. The carrier fluid then proceeds to the Pelton wheel where it is dropped in pressure. This process recovers energy that is used to help offset the energy required by the pump. The carrier fluid

is now at the absorber pressure but it is at a higher temperature than the absorber. This is due to the fact that a real heat exchanger has an effectiveness of less than one. Ideally the regenerated carrier fluid should leave the heat exchanger at the temperature at which the mixture is entering. However, it leaves at a slightly higher temperature and it is this temperature difference that must be removed by the carbonate cooler.

The carbonate cooler is simply a heat exchanger. The excess heat is transferred from the carrier fluid to cooling water. In the case of the binary cycle, the cooling water is sea water that is used for desalination. The carrier fluid, now at the absorber temperature and pressure, returns to the absorber and the cycle continues.

No mention is made of regeneration, reheat or any other efficiency improving methods in this cycle, however, they could easily be employed. They are not included in this report for reasons of simplicity. Addition of one or more of these methods to the cycle would improve the efficiency.

Although CO_2 is used as the working fluid in the turbine,

any gas that can be absorbed by the carrier fluid could be used. It has an advantage over steam in that it has a very low point of vaporization and there is virtually no danger of liquid droplets damaging the turbine blades. Some water vapor would be present in the CO_2, however, and the turbine outlet conditions would have to be selected so that the vapor did not condense in the turbine.

The CO_2 cycle offers several advantages over conventional power cycles. The increased efficiency will mean a lower fuel requirement for the same amount of electrical output or an increased electrical output with the same fuel input. In other words, a barrel of oil will result in a greater output of electrical power.

Another advantage is that heat is rejected from the absorber, due to the heat of reaction of the absorption process, and it can be used to heat sea water for desalination. The heat from the absorber can be given off at a high enough temperature to produce a substantial amount of fresh water while generating power at an efficiency higher than that of a conventional Rankine cycle.

A decrease in thermal pollution will also be realized over

conventional power plants. Conventional plants must reject heat from the condenser where the steam from the turbine is changed to water. This heat is removed by cooling water which is allowed to flow to a body of water where the heat is dumped. The cooling water, after passing over the condenser, is generally at a temperature of 90-100°F (32.2-37.8°C) and is a source of thermal pollution. The waste heat from the CO_2 cycle is used in the desalination plant to desalt sea water. The heat from the CO_2 cycle is at a high enough temperature that desalination is feasible whereas the heat from a conventional condenser is not. It should be noted, that heat is rejected from the desalination plant via the brine that is rejected to control salinity. The temperature of this brine, however, is lower than that of the cooling water from the condenser and it thus poses a lesser threat of thermal pollution.

CHAPTER 3

THERMODYNAMIC ANALYSIS

3.1 Introduction

The thermodynamic equations for each device are derived based on Figure 3.1. Each device is treated separately and the appropriate assumptions are stated for each. A discussion of other assumptions and equations is presented at the end of the chapter.

To facilitate changes in numerical values and the many calculations required to obtain the desired data with each change, a computer program was written. The equations presented here are the same equations used in the program. The program and a brief explanation are presented in Appendix B.

3.2 Absorber

The absorber performs the job of combining the CO_2 from the turbine with the carrier fluid. This is accomplished by an absorption process in which the CO_2 is absorbed by the carrier fluid. The absorption process occurs by way

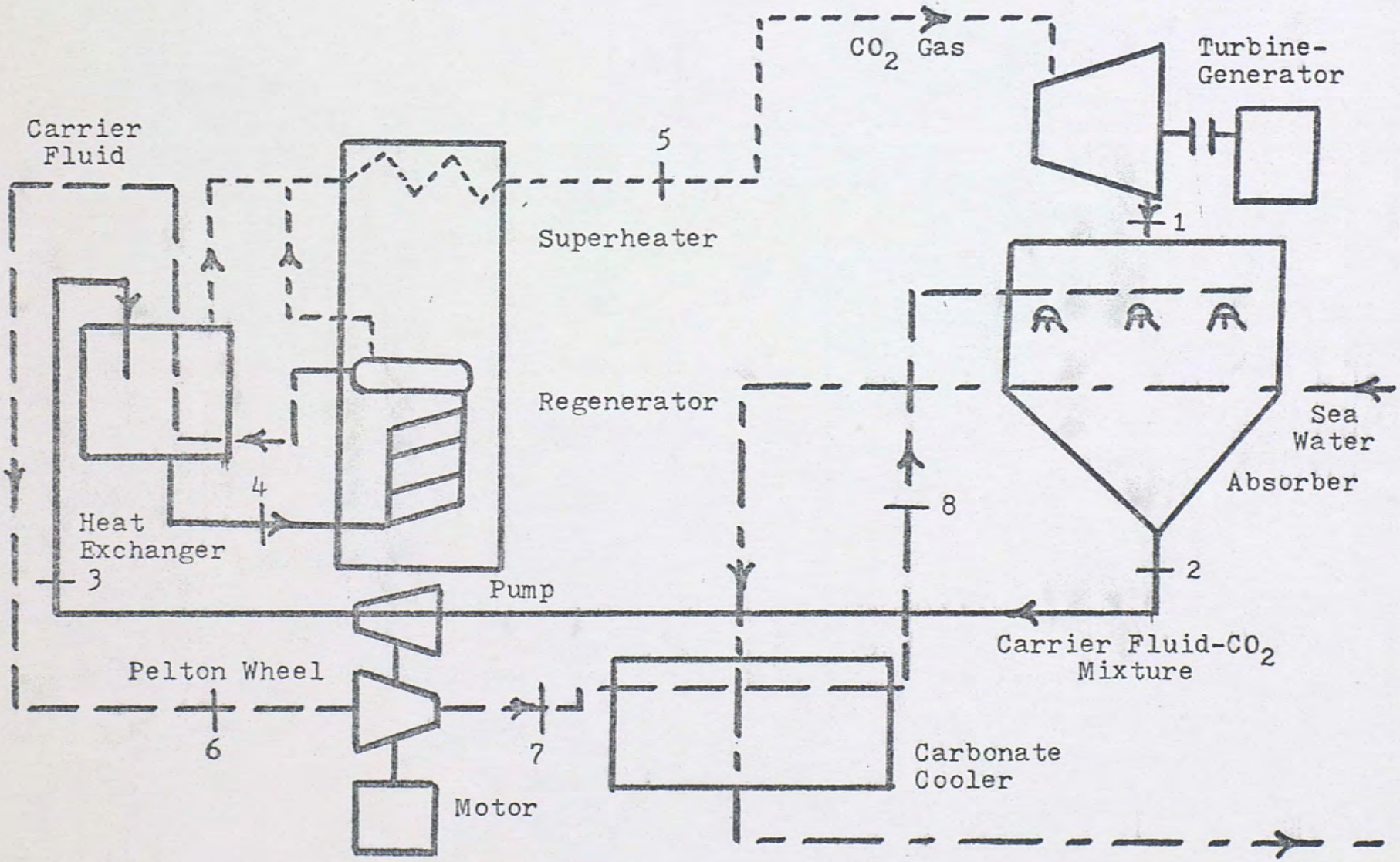

FIGURE 3.1 - CO_2 Absorption Power Generation Cycle for Analysis

of an exothermic chemical reaction. The exothermic reaction implies a heat loss associated with this device which is simply the heat of reaction, hor, of the two compounds and can be found in a table of heats of reaction[4]. The total heat lost per unit time is the mass flow rate of the CO_2 times the heat of reaction. That is:

$$Q_{abs} = \dot{m}_{CO_2} \cdot hor \qquad (3.1)$$

Where Q_{abs} = Heat loss per unit time from the absorber

hor = Heat of reaction given in BTU per pound of CO_2 absorbed

$\dot{m}_{CO_2}$ = Mass flow rate of CO_2

Several assumptions are made about the absorber to apply it to the CO_2 cycle. It is assumed that the absorption efficiency is 100%. In other words, all the CO_2 that enters the chamber is absorbed by the carrier fluid and the carrier fluid absorbs to its maximum capacity. Practically, the absorption efficiency ranges up to about 80% in a conventional absorption-regeneration process.

An assumption is also made about the absorber pressure. In conventional absorption-regeneration processes, the

absorber pressure is usually around 300 psig. While the carrier fluids have a natural tendency to absorb CO_2, the high pressure acts as a driving force to enhance absorption of CO_2 by the carrier fluid. The operating pressure for the absorber in the CO_2 cycle, however, is 25 psia. The pressure is maintained this low to get more power from the turbine. This low pressure may well have an adverse effect on the absorption rate.

It is further assumed that any adverse effect on the absorption capacity caused by the low pressure in the absorber can be offset by the fact that pure CO_2 is being absorbed, improving the carrying capacity of the fluid. A similar result is obtained from experiment in reference 5. In these experiments, an increase in the CO_2 content of the feed gas in the absorber, in general, caused an increase in the carrying capacity of the fluid.

In the calculations performed in this report, it is assumed that the absorber temperature is equal to the outlet temperature of the turbine and all the heat generated by the absorption process is used to heat sea water for desalination. If the desalting process were not included in this cycle, the liberated heat could be used to reheat

the gas leaving the turbine. The gas in the turbine could then be expanded to a very low temperature, producing more work, and then heated to the temperature necessary for absorption by the heat of reaction given off. There is, however, a Second Law of Thermodynamics limitation due to the fact that at certain conditions, Carnot efficiency is exceeded. However, since this facet of the cycle does not deal with the binary aspects, it is not discussed in this report.

3.3 Pump and Pelton Wheel

The pump raises the pressure of the mixture coming from the carbonate cooler to the pressure at which it will enter the turbine. Constant pressure is assumed across the regenerator-superheater and the necessary turbine inlet pressure must be realized by the pump. The work performed by the pump is a compression process described by:

$$w_p = \int v dP + \int P dv \qquad (3.2)$$

Where w_p = Work of the pump per unit mass

v = Specific volume

P = Pressure

If the carrier fluid is assumed incompressible, the volume

does not change and Equation 3.2 reduces to:

$$w_p = v\int dP \tag{3.3}$$

Integrating between points 2 and 3 and recognizing that the specific volume is that of the carrier fluid-CO_2 mixture:

$$w_p = v_{mix}(P_3 - P_2) \tag{3.4}$$

Where v_{mix} = Specific volume of the carrier fluid-CO_2 mixture

Multiplying by the mass flow rate of the mixture:

$$W_p = \dot{m}_{mix} v_{mix}(P_3 - P_2) \tag{3.5}$$

Where $\dot{m}_{mix}$ = Mass flow rate of the carrier fluid-CO_2 mixture

W_p = Pump work per unit time

The Pelton wheel extracts energy from the hot, high pressure, regenerated carrier fluid returning to the absorber. The high pressure fluid is allowed to expand through the Pelton wheel, extracting energy to offset some of the energy required by the pump. Constant temperature is assumed across the Pelton wheel and, therefore, while the

pressure drops, the temperature remains the same.

The analysis for the Pelton wheel is similar to that of the pump except, in this case, a decrease in pressure is involved as opposed to an increase in pressure across the pump. Equation 3.3 again results, but this time the work is being done by the fluid on the device instead of the device doing the work on the fluid as in the case of the pump. As before:

$$w_{pw} = v\int dP \qquad (3.6)$$

Where w_{pw} = Work of the Pelton wheel per unit mass

The work is produced between points 6 and 7 as shown in Figure 3.1. Recognizing that the fluid at these points is the carrier fluid, Equation 3.6 reduces similarly as before:

$$W_{pw} = \dot{m}_{car} v_{car} (P_7 - P_6) \qquad (3.7)$$

Where $\dot{m}_{car}$ = Mass flow rate of the carrier fluid

v_{car} = Specific volume of the carrier fluid

W_{pw} = Pelton wheel work per unit time

Bringing a negative sign out in front of Equation 3.7

to reverse the pressures and adding it to Equation 3.5, an equation for the net energy required by the pump-Pelton wheel combination is:

$$W_{tot} = \dot{m}_{mix} v_{mix} (P_3 - P_2) - \dot{m}_{car} v_{car} (P_6 - P_7) \qquad (3.8)$$

Where W_{tot} = Net power required by the pump-Pelton wheel combination

Inserting the efficiencies of the pump and Pelton wheel, the net power becomes:

$$W_{tot} = \frac{\dot{m}_{mix} v_{mix} (P_3 - P_2)}{\eta_p} - \dot{m}_{car} v_{car} (P_6 - P_7) \eta_{pw} \qquad (3.9)$$

Where η_p = Efficiency of the pump

η_{pw} = Efficiency of the Pelton wheel

The pressure rise across the pump is assumed equal to the pressure drop across the Pelton wheel. That is:

$$(P_3 - P_2) = (P_6 - P_7) \qquad (3.10)$$

Using Equation 3.10 and assuming that the specific volume

of the mixture is equal to the specific volume of the carrier fluid (They are within 6%, see Section 3.8), Equation 3.9 reduces to:

$$W_{tot} = v_{mix}(P_3 - P_2)\left(\frac{\dot{m}_{mix}}{\eta_p} - \dot{m}_{car}\eta_{pw}\right) \qquad (3.11)$$

This is an equation for the net power required by the pump-Pelton wheel combination.

The power required by the pump will be greater than that supplied by the Pelton wheel, due to the fact that the mass flow rate of the carrier fluid-CO_2 mixture is greater then that of the carrier fluid. Equation 3.11 is an indication of the net power that must be added to power the pump.

3.4 Carbonate Cooler

The carbonate cooler, is simply a heat exchanger that recovers some of the energy from the carrier fluid returning to the absorber from the regenerator. Most of the heat is removed from the carrier fluid by the regenerator heat exchanger. Ideally, the regenerated carrier fluid should leave the heat exchanger at the same temperature at which the carrier fluid-CO_2 mixture enters. However, due to inefficiencies, the carrier fluid does not transfer all

its heat to the mixture and it leaves the heat exchanger at a slightly higher temperature than the entering mixture. This temperature is also slightly higher than the absorber temperature. To reduce the temperature, the carrier fluid is piped through the carbonate cooler, where it gives up heat to cooling water flowing through the device. In the binary cycle, this cooling water is sea water for desalination.

The heat loss by the carrier fluid is the enthalpy difference times the mass flow rate. That is:

$$Q_{cool} = \dot{m}_{car}(h_7 - h_8) \qquad (3.12)$$

Where Q_{cool} = Heat lost in the carbonate cooler per unit time

$\dot{m}_{car}$ = Mass flow rate of the carrier fluid

h_7 = Enthalpy of the carrier fluid entering the carbonate cooler

h_8 = Enthalpy of the carrier fluid leaving the carbonate cooler

Assuming that $(h_7 - h_8)$ can be approximated by $c_p(T_7 - T_8)$ (see Appendix A.1), where c_p is the specific heat of the carrier fluid and T_7 and T_8 are the temperatures entering

and leaving the carbonate cooler, respectively, Equation 3.12 can be written:

$$Q_{cool} = \dot{m}_{car} c_p (T_7 - T_8) \qquad (3.13)$$

This equation specifies the amount of heat lost by the carbonate cooler.

It is assumed, for the purpose of this study, that the temperature difference across the carbonate cooler is ten degrees. This implies that the regenerator heat exchanger transfers enough heat from the returning carrier fluid to the carrier fluid-CO_2 mixture, to where the carrier fluid leaving is only ten degrees higher in temperature than the mixture entering. Current heat exchanger technology is adequate to produce a device with this performance.

3.5 Turbine-Generator

The electrical power generation in the CO_2 cycle is by a conventional turbine and generator. The rated output of the turbine is assumed constant at 1000 kilowatts. The inlet and outlet turbine temperatures are specified as is the outlet pressure. The inlet pressure is calculated by assuming isentropic flow through the turbine and using

the isentropic equations. Calculations are also performed to obtain the turbine work and the required CO_2 flow rate. The equations are derived as follows:

The work of the turbine is the enthalpy difference across it:

$$w_t = (h_5 - h_1) \tag{3.14}$$

Where w_t = Work of the turbine per unit mass

h = Enthalpy at the point subscripted

Assuming that CO_2 acts as an ideal gas, and approximating the enthalpy difference by the specific heat times the corresponding temperature difference (see Appendix A.2):

$$(h_5 - h_1) = c_p(T_5 - T_1) \tag{3.15}$$

Substituting Equation 3.15 into Equation 3.14:

$$w_t = c_p(T_5 - T_1) \tag{3.16}$$

The power generated is the CO_2 mass flow rate times the turbine work:

$$W_t = w_t \dot{m}_{CO_2} \tag{3.17}$$

Where $\dot{m}_{CO_2}$ = Mass flow rate of the CO_2

W_t = Power generated (1000 kw)

Rearranging Equation 3.17:

$$\dot{m}_{CO_2} = \frac{W_t}{w_t} \tag{3.18}$$

Equations 3.16 and 3.18 specify the required CO_2 mass flow rate necessary to generate the specified power output at the given inlet and exit temperatures.

Once the CO_2 mass flow rate is found, knowing the ratio of pounds of carrier fluid circulated per pound of CO_2 absorbed (henceforth referred to as ratio), the mass flow rate of the carrier fluid can be found:

$$\dot{m}_{car} = R\dot{m}_{CO_2} \tag{3.19}$$

Where $\dot{m}_{car}$ = Mass flow rate of the carrier fluid

R = Ratio of pounds of carrier fluid circulated per pound of CO_2 absorbed

The turbine inlet pressure is calculated by use of isentropic relations across the turbine. The actual turbine work is given by Equation 3.16. To determine the isen-

tropic work, Equation 3.16 is divided by the efficiency of the turbine:

$$w_{ts} = \frac{w_t}{\eta_t} \tag{3.20}$$

Where w_{ts} = Isentropic turbine work per unit mass

η_t = Turbine efficiency

The isentropic turbine work can also be found by a relation similar to Equation 3.16:

$$w_{ts} = c_p(T_5 - T_{1s}) \tag{3.21}$$

Where T_{1s} = Temperature at exit to the turbine if isentropic expansion occurs

Solving for T_{1s}:

$$T_{1s} = -\frac{w_{ts}}{c_p} + T_5 \tag{3.22}$$

Once a value for isentropic turbine work is obtained from Equation 3.20, Equation 3.22 is used to determine the isentropic turbine outlet temperature. The relationship between temperature and pressure for an isentropic process is given by:

$$\frac{P_1}{P_5} = \left(\frac{T_{1s}}{T_5}\right)^{\frac{c_p}{\mathbb{R}}} \qquad (3.23)$$

Where P_1 = Turbine exit pressure

P_5 = Turbine inlet pressure

$\mathbb{R}$ = Gas constant

Solving for P_5:

$$P_5 = P_1 / \left(\frac{T_{1s}}{T_5}\right)^{\frac{c_p}{\mathbb{R}}} \qquad (3.24)$$

Equation 3.24 determines the inlet turbine pressure given the inlet temperature and the outlet temperature and pressure.

3.6 Regenerator-Superheater

The regenerator and superheater are actually two devices, but the heat used by each is calculated as one quantity. In the regenerator, the bulk of the CO_2 is liberated from the carrier fluid. It then goes to the superheater, where it is heated to the temperature at which it will enter the turbine.

The regenerator and superheater are immediately preceeded by a heat exchanger. The heat exchanger transfers heat

from the hot, regenerated carrier fluid, from which the CO_2 has been liberated, to the cool incoming carrier fluid-CO_2 mixture. This heat is transferred within the cycle and is thus, neither a loss nor gain to the cycle (neglecting inefficiencies). Its benefit is reflected in the fact that it preheats the mixture, causes a small amount of CO_2 to be released and initiates the regeneration process.

The heat required by the two devices can be calculated by writing a heat balance for the cycle:

$$\text{Energy in} = \text{Energy out} \tag{3.25}$$

The energy into the system is the net work of the pump-Pelton wheel combination and the heat required by the regenerator-superheater. The energy out is the absorber heat loss, the carbonate cooler heat loss and the turbine power generated. Equation 3.25 becomes:

$$W_{tot} + Q_{rs} = Q_{abs} + Q_{cool} + W_t \tag{3.26}$$

Where Q_{rs} = Heat required by the regenerator-superheater

Solving for Q_{rs}:

$$Q_{rs} = Q_{abs} + Q_{cool} + W_t - W_{tot} \tag{3.27}$$

Equation 3.27 determines the amount of heat required by the regenerator-superheater since the quantities on the right side of the equation are known from previous calculations.

One assumption has to be made for the regenerator. Practically, the operating pressure of the regenerator is less than 39 psia. According to reference 5, the best pressure is subatmospheric at about 11.2 psia. In the CO_2 cycle, the carrier fluid-CO_2 mixture goes through the pump immediately before entering the regenerator and is elevated to a high pressure desired for entrance to the turbine (1000-2000 psia). It is assumed that this high pressure does not adversely affect the regeneration of the carrier fluid. This assumption can be supported by the following reasoning:

Regeneration is basically a boiling process (there is also a chemical compound breakdown). The carrier fluid-CO_2 mixture is raised to its boiling temperature for the pressure at which the regenerator is maintained, and the CO_2 is boiled off, leaving the carrier fluid. If the pressure of the solution in the regenerator is approaching 2000 psia, then the solution must be heated to the corresponding

boiling temperature, for this pressure, to liberate the CO_2. The high pressure would, therefore, not seem to be a problem in that all that is necessary to release the CO_2, is raise the temperature to the corresponding boiling temperature. However, further work is necessary to determine if this temperature is low enough to be feasible with current boiler technology.

A graph is produced in reference 5 of boiling temperature versus regenerator pressure for a 30% and a 40% original potassium carbonate solution (in other words, the percentage before the CO_2 is absorbed). This graph, however, only goes as high as 35 psia, much lower than the regeneration pressures proposed in this cycle. An extrapolation of the curves is done to determine the approximate boiling temperature for these pressures. This extrapolation is shown in Figure 3.2. The curves presented in reference 5 are very similar to the temperature versus pressure curve for water. This is logical, in that the solutions are respectively 70% and 60% water. The curves are extrapolated on this basis.

The turbine inlet pressure, which is the same as the regenerator pressure, is given for different turbine out-

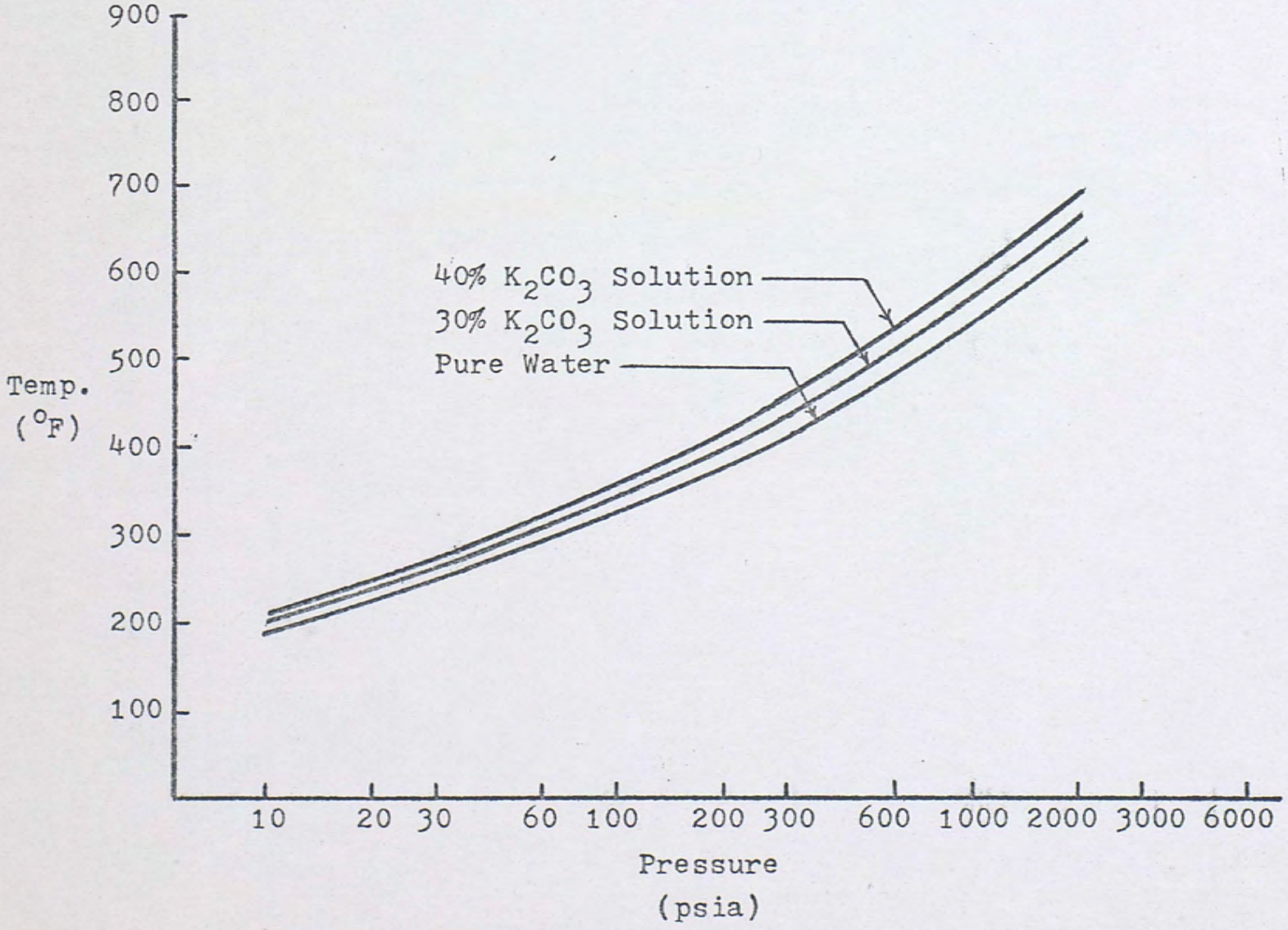

FIGURE 3.2 - Potassium Bicarbonate Boiling Temperature

let temperatures, as calculated by isentropic conditions, in Table 4.2 on page 41. From the table, the highest pressure reached by the CO_2 cycle is less than 1400 psia. Returning to Figure 3.2, this corresponds to a boiling temperature of less than 650°F (343.3°C). With respect to current boiler technology, this is not a high temperature. From Figure 3.2, even if the pressure is as high as 2000 psia, the corresponding boiling temperature is only about 700°F (371.1°C). Regeneration temperatures necessary for the high pressure encountered in the CO_2 cycle are, therefore, reasonable and feasible.

With the high temperature necessary for boiling the solution at these high pressures, much of the heat required by the regenerator-superheater combination will be used by the regenerator in liberating the CO_2. However, the CO_2, in regeneration, will acquire heat and leave the regenerator at approximately the regenerator temperature. It will, therefore, be preheated when it enters the superheater and less heat will be needed by the superheater to heat it to its final temperature for entrance to the turbine.

3.7 Cycle Efficiency

The cycle efficiency is given by the relation:

$$\eta = \frac{W_{net}}{Q_{added}} \tag{3.28}$$

Where Q_{added} = Total heat added to the cycle

W_{net} = Net work in the cycle

η = Cycle efficiency

The net work is given by the difference between the work input to the cycle and the work output of the cycle. The work output of the cycle is the work of the turbine, while the work input to the cycle is the net work required by the pump-Pelton wheel combination. The heat added to the cycle is the heat supplied to the regenerator and super-heater. Equation 3.28 becomes:

$$\eta_{CO_2} = \frac{W_t - W_{tot}}{Q_{rs}} \tag{3.29}$$

Equation 3.29 determines the CO_2 cycle efficiency.

Examining the quantities in Equation 3.27, the turbine work is assumed constant for the different conditions and different carrier fluids examined in this study, and the

net work required by the pump and Pelton wheel is very small (Table 4.2). Therefore, changes in the heat from the carbonate cooler and the absorber, to a large extent, will control the amount of heat added to the regenerator-superheater and thus, the system. Examining Equation 3.29, a change in the amount of heat added to the system will have an inverse effect on the cycle efficiency. An increase in the heat added will lower the efficiency, while a decrease in the heat added will increase the efficiency. Since a change in the amount of heat added to the system is controlled by the change in heat from the carbonate cooler and the absorber, these two devices will be the dominant efficiency factors in considering different carrier fluids. In other words:

$$\eta \propto \frac{1}{Q_{cool} + Q_{abs}} \qquad (3.30)$$

The efficiency discussed throughout this report is the efficiency of the CO_2 cycle and excludes the desalting process. No attempt is made in defining an overall power generation salt water distillation cycle efficiency.

3.8 Discussion

For the four fluids investigated the specific volume of

the carrier fluid was assumed equal to the specific volume of the carrier fluid-CO_2 mixture. For potassium carbonate, which had the highest ratio of fourteen, this was a good assumption. The addition of one part of CO_2 to fourteen parts of carbonate, will not change the specific volume by a significant amount. This can be verified with data from references 5 and 6.

The specific volume of a 24% solution of potassium carbonate at 60.8°F (16°C) is .0130 ft^3/lb_m. The specific volume of a 24% solution of potassium bicarbonate at 60.8°F (16°C) is .0137 ft^3/lb_m (potassium bicarbonate is the result of potassium carbonate absorbing CO_2). The difference in the two is approximately 6%. The concentrations and temperatures in this comparison are not the same as the actual conditions encountered in the cycle due to the scarcity of data for the specific volume of potassium bicarbonate. The above concentration is the highest available and is for the temperature given. It is assumed that a similar result would be obtained at the desired temperature and concentration. Data was also available to compare sodium hydroxide and sodium bicarbonate (the result of sodium hydroxide absorbing CO_2) and a similar conclusion is reached about the specific

volumes (this data was also at low concentrations). It is assumed that the same conclusion is valid for all the carrier fluids.

In the case of the fluids with a high heat of reaction and a low ratio, this assumption, whether valid or not, is of no consequence. With a low ratio, the carrier fluid-CO_2 mixture mass flow rate is low and the pump work is small when compared with the other quantities in the system. Similarly, the energy recovered by the Pelton wheel is also small in comparison with the other quantities. These two quantities are the only ones that are functions of the carrier fluid and the carrier fluid-CO_2 mixture. While a change in the assumption that the specific volume of the carrier fluid is equal to the specific volume of the carrier fluid-CO_2 mixture could cause considerable change in the net energy required by the pump-Pelton wheel combination, the effect on the cycle efficiency would be negligible.

The Carnot cycle efficiency is also calculated as a point of comparison. The Carnot efficiency is the maximum efficiency that could possibly be obtained from the cycle and is calculated as follows:

$$\eta_{Carnot} = \frac{T_h - T_l}{T_h} \qquad (3.31)$$

Where η_{Carnot} = Carnot efficiency

T_h = Highest temperature in the cycle in absolute units

T_l = Lowest temperature in the cycle in absolute units

The equations derived in this chapter are the equations used in the computer program presented in Appendix B. Appropriate assumptions have been made to simplify the analysis. The results of the calculations, using the above equations and the appropriate data for each fluid, are presented in Chapter 4.

CHAPTER 4

CARRIER FLUIDS

4.1 Introduction

Four fluids are considered as possible carrier fluids for the CO_2; potassium carbonate, sodium hydroxide, lithium hydroxide and the ethanolamines. These are some of the more popular and/or well studied carrier fluids in use in conventional absorption-regeneration systems. There are, however, other carrier fluids being used.

The data for each fluid is presented along with the source from which it came. The validity of some of the data is questionable, but in all cases, the most reasonable value for each specific piece of data was used. The data was assumed to have a constant value for all conditions of temperature and pressure. Most of the data, typically, the ratio, varies with temperature and pressure. It was assumed that this variation was insignificant.

It should be noted, that the lowest turbine outlet temperature for which results are obtained is 180°F (82.2°C).

Due to the fact that the turbine outlet temperature is equal to the absorber temperature and the sea water for desalination is heated by the absorber heat, assuming no losses, the sea water is heated to the same temperature as the turbine outlet. Temperatures less than $180^{\circ}F$ are not practical for sea water desalting.

4.2 Potassium Carbonate

Potassium carbonate is one of the most popular and well studied carrier fluids being used in conventional absorption-regeneration processes. It has a good absorption capacity (low ratio) and requires relatively little heat for regeneration.

The governing chemical reaction for absorption of CO_2 by potassium carbonate is as follows:

$$K_2CO_3 + H_2O + CO_2 \rightleftharpoons 2KHCO_3 \qquad (4.1)$$

An aqueous solution of potassium carbonate combines with CO_2 in the absorber to form potassium bicarbonate. This fluid flows to the regenerator, where the CO_2 is separated from the potassium carbonate. The CO_2 proceeds to the superheater and the potassium carbonate returns to the absorber to absorb more CO_2.

The data for potassium carbonate which was used in the thermodynamic analysis is given in Table 4.1. An abundant supply of data was available, however, several different values were obtained for each quantity from different sources due to differing assumptions and/or experimental conditions. Three values of ratio were available. A value of 11 pounds of carrier fluid to pounds of CO_2 is obtained from theoretical calculations, with data from the Critical Tables[4] (see Appendix A.3). A value of 23 is obtained from experiment with absorption-regeneration equipment[5] and a value of 42 is obtained from data for hot carbonate used to scrub flue gases with low partial pressures of CO_2[5]. The value of ratio used in the calculations was 14. Although 23 is the value obtained from experiment, the fact that pure CO_2 is being absorbed should enhance the absorption characteristics (Section 3.2) of the potassium carbonate.

Two values of heat of reaction were available. The theoretical value of 77 BTU per pound, calculated with data from the Critical Tables[4] (see Appendix A.4) and a value of 231 obtained from reference 5. The theoretical value of 77 BTU per pound is obtained using the heat of formation of wet CO_2 (CO_2 and water vapor). The 231 BTU

TABLE 4.1

CARRIER FLUID DATA

Carrier Fluid	Heat of Reaction	Ratio	Specific Heat	Specific Volume
	$\frac{BTU}{lb_m}$	$\frac{\text{pounds of carrier fluid}}{\text{pound of } CO_2 \text{ absorbed}}$	$\frac{BTU}{lb_m}$	$\frac{ft^3}{lb_m}$
K_2CO_3	77	14	.75	.0126
K_2CO_3	157	14	.75	.0126
K_2CO_3	231	14	.75	.0126
NaOH	1146.85	.9091	.93	.0121
LiOH	876.22	1.25	.96	.01097
RNH_2	828.29	2.13	.90	.0146

per pound value is an experimental value obtained from experiments conducted with an absorption-regeneration system pilot plant. Both values of heat of reaction were used in the calculations as was a value of 157 BTU per pound. This last value is approximately midway between the other two values. Due to the wide discrepancy between the theoretical and practical values, 157 was used to obtain a parameter range. The specific volume and specific heat were obtained from reference 7.

The results of the calculations for potassium carbonate are presented in Figure 4.1 and Table 4.2. The obvious advantage of a potassium carbonate cycle over the average Rankine cycle is the efficiency. Depending on the turbine outlet temperature and the value of the heat of reaction, the efficiency varies from 29% to 44%. Even in the worst case, the CO_2 cycle generates electricity at an efficiency only 1% less than the average conventional Rankine cycle (30%). At the same time, it is generating a substantial amount of fresh water. It should be noted, that the average conventional Rankine cycle usually includes at least one of several efficiency improving methods now available. The calculations for the CO_2 cycle include none of these methods. If the effects of these methods

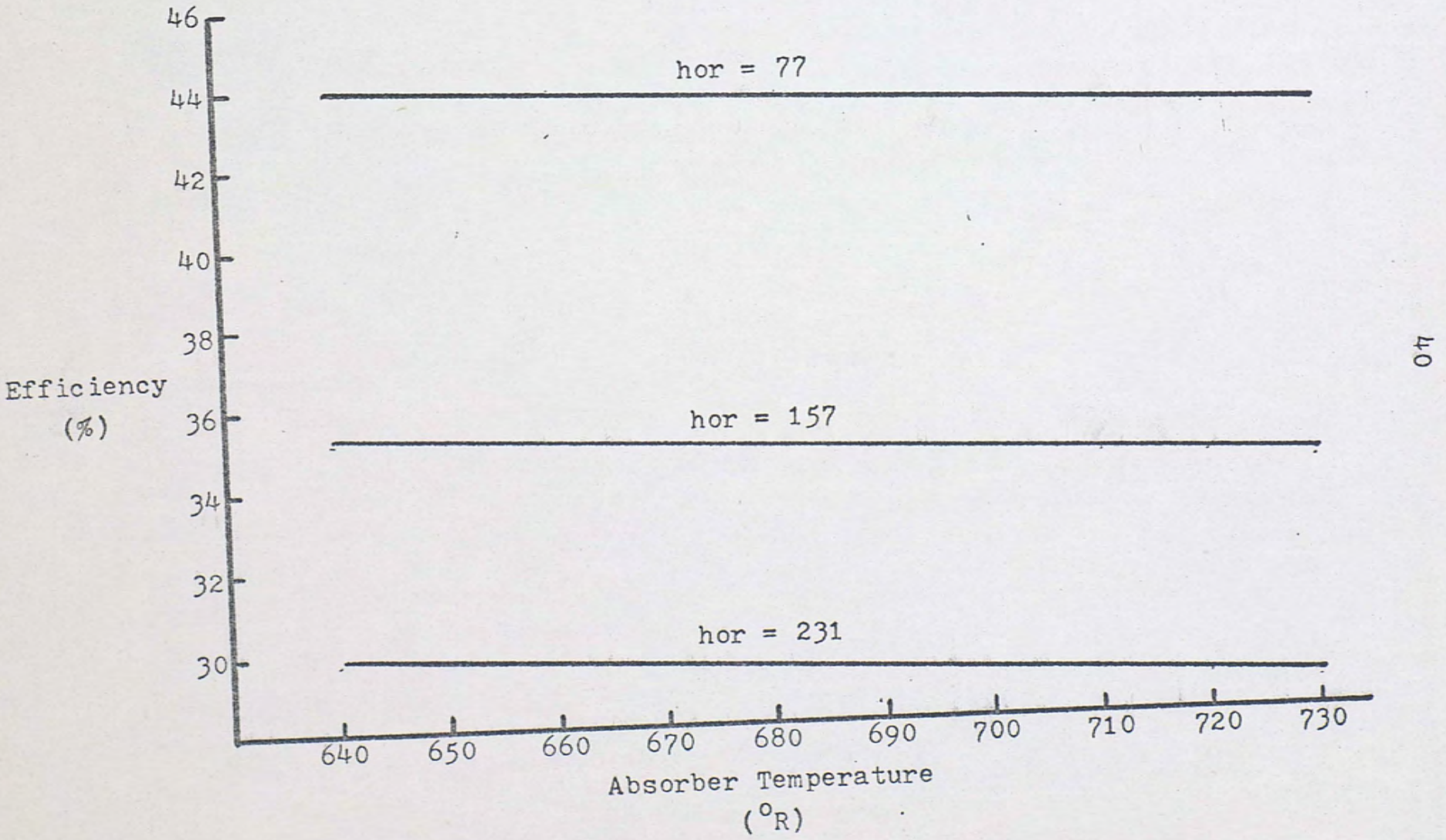

FIGURE 4.1 - CO_2 Cycle Efficiency for K_2CO_3

TABLE 4.2.1

RESULTS OF CO_2 CYCLE CALCULATIONS, POTASSIUM CARBONATE

T_{out} (^oR)	640	650	660	670	680
T_{in} (^oR)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	1373.9	1270.5	1176.4	1090.6	1012.5
$\dot{m}_{CO2}$ (lb_m/hr)	20598.9	20853.2	21113.8	21381.1	21655.2
R (lb_{car}/lb_{CO2})	14	14	14	14	14
hor (BTU/lb_m)	77	77	77	77	77
Q_{abs} (BTU/hr)	1586113.0	1605695.0	1625767.0	1646346.0	1667453.0
W_p (BTU/hr)	1214812.0	1135467.0	1062793.0	996119.1	934854.1
W_{tot} (BTU/hr)	489164.0	457214.3	427951.4	401104.3	376434.0
Q_{cool} (BTU/hr)	2162881.0	2189584.0	2216955.0	2245017.0	2273800.0
Q_{rs} (BTU/hr)	6670970.0	6749195.0	6825892.0	6901372.0	6975927.0
η_{Carnot}	.562	.555	.548	.541	.534
η_{CO2}	.438	.438	.437	.436	.435

TABLE 4.2.1 (Continued)

RESULTS OF CO_2 CYCLE CALCULATIONS, POTASSIUM CARBONATE

T_{out} (^oR)	690	700	710	720	730
T_{in} (^oR)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	941.0	875.6	815.7	760.7	710.2
$\dot{m}_{CO2}$ (lb_m/hr)	21936.5	22228.1	22521.4	22825.8	23138.5
R (lb_{car}/lb_{CO2})	14	14	14	14	14
hor (BTU/lb_m)	77	77	77	77	77
Q_{abs} (BTU/hr)	1689108.0	1711333.0	1734150.0	1757585.0	1781662.0
W_p (BTU/hr)	878470.4	826503.7	778539.1	734205.2	693171.3
W_{tot} (BTU/hr)	353730.9	332805.6	313492.2	295640.4	279117.2
Q_{cool} (BTU/hr)	2303329.0	2333636.0	2364750.0	2396707.0	2429539.0
Q_{rs} (BTU/hr)	7049807.0	7123257.0	7196495.0	7269735.0	7343162.0
η_{Carnot}	.527	.521	.514	.507	.500
η_{CO2}	.434	.432	.430	.429	.427

TABLE 4.2.2

RESULTS OF CO_2 CYCLE CALCULATIONS, POTASSIUM CARBONATE

T_{out} (^oR)	640	650	660	670	680
T_{in} (^oR)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	1373.9	1270.5	1176.4	1090.6	1012.4
$\dot{m}_{CO_2}$ (lb_m/hr)	20598.9	20853.2	21113.9	21381.1	21655.2
R (lb_{car}/lb_{CO_2})	14	14	14	14	14
hor (BTU/lb_m)	157	157	157	157	157
Q_{abs} (BTU/hr)	3234023.0	3273951.0	3314875.0	3356835.0	3399873.0
W_p (BTU/hr)	1214812.0	1135467.0	1062793.0	996119.1	934854.1
W_{tot} (BTU/hr)	489164.0	457214.3	427951.4	401104.3	376434.9
Q_{cool} (BTU/hr)	2162881.0	2189584.0	2216955.0	2245017.0	2273800.0
Q_{rs} (BTU/hr)	8318880.0	8417451.0	8515000.0	8611861.0	8708347.0
η_{Carnot}	.562	.555	.548	.541	.534
η_{CO_2}	.351	.351	.350	.350	.350

TABLE 4.2.2 (Continued)

RESULTS OF CO_2 CYCLE CALCULATIONS, POTASSIUM CARBONATE

T_{out} (^oR)	690	700	710	720	730
T_{in} (^oR)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	941.0	875.6	815.7	767.3	710.2
$\dot{m}_{CO_2}$ (lb_m/hr)	21936.5	22225.1	22521.4	22825.8	23138.5
R (lb_{car}/lb_{CO_2})	14	14	14	14	14
hor (BTU/lb_m)	157	157	157	157	157
Q_{abs} (BTU/hr)	3444026.0	3489342.0	3535865.0	3583648.0	3632740.0
W_p (BTU/hr)	878470.4	826503.8	778539.1	734305.2	693171.3
W_{tot} (BTU/hr)	353730.9	332805.6	313492.3	295640.4	279117.3
Q_{cool} (BTU/hr)	2303329.0	2333636.0	2364750.0	2936707.0	2429539.0
Q_{rs} (BTU/hr)	8804725.0	8901266.0	8998210.0	9095798.0	9194240.0
η_{Carnot}	.527	.521	.514	.507	.500
η_{CO_2}	.347	.346	.344	.343	.341

TABLE 4.2.3

RESULTS OF CO_2 CYCLE CALCULATIONS, POTASSIUM CARBONATE

T_{out} (^oR)	640	650	660	670	680
T_{in} (^oR)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	1373.9	1270.5	1176.4	1090.7	1012.4
$\dot{m}_{CO2}$ (lb_m/hr)	20598.9	20853.2	21113.9	21381.1	21655.2
R (lb_{car}/lb_{CO2})	14	14	14	14	14
hor (BTU/lb_m)	231	231	231	231	231
Q_{abs} (BTU/hr)	4758340.0	4817087.0	4877301.0	4939038.0	5002360.0
W_p (BTU/hr)	1214812.0	1135467.0	1062793.0	996119.1	934854.1
W_{tot} (BTU/hr)	489164.0	457214.3	427951.4	401104.3	376434.9
Q_{cool} (BTU/hr)	2162881.0	2189584.0	2216955.0	2245017.0	2273800.0
Q_{rs} (BTU/hr)	9843197.0	9960587.0	10077426.0	10194064.0	10310834.0
η_{Carnot}	.562	.555	.548	.541	.534
η_{CO2}	.297	.297	.296	.295	.294

TABLE 4.2.3 (Continued)

RESULTS OF CO_2 CYCLE CALCULATIONS, POTASSIUM CARBONATE

T_{out} (^{o}R)	690	700	710	720	730
T_{in} (^{o}R)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	941.0	875.6	815.7	760.7	710.2
$\dot{m}_{CO_2}$ (lb_m/hr)	21936.5	22225.1	22521.4	22825.8	23138.5
R (lb_{car}/lb_{CO_2})	14	14	14	14	14
hor (BTU/lb_m)	231	231	231	231	231
Q_{abs} (BTU/hr)	5067326.0	5134000.0	5292452.0	5272757.0	5344987.0
W_p (BTU/hr)	878470.4	826503.8	778539.1	734205.2	693171.3
W_{tot} (BTU/hr)	353730.9	332805.6	313492.3	295640.4	279117.3
Q_{cool} (BTU/hr)	2303321.0	2333636.0	2364750.0	2396707.0	2429539.0
Q_{rs} (BTU/hr)	10428025.0	10545924.0	10664797.0	10784907.0	10906487.0
η_{Carnot}	.527	.521	.514	.507	.500
η_{CO_2}	.293	.292	.290	.289	.287

were considered (they normally increase the efficiency by several per cent), the CO_2 cycle efficiency would in all cases be better than the 30% efficiency of the average Rankine Cycle. (A Rankine cycle without these methods included is examined in Section 5.6).

As stated previously, the lowest turbine outlet temperature considered in this report is 180°F. This is due to the fact that lower temperatures do not promote efficient operation of the desalination process. Although the effects are not discussed in this report, it is obvious that a lower turbine outlet temperature, disregarding the desalination plant, would improve the cycle efficiency.

4.3 Ethanolamines

4.3.1 Monoethanolamine

Monoethanolamine is used in some conventional commercial processes for removing CO_2 (and other gases) from gas streams. It's strong point for use is that it has a high absorption capacity (low ratio). It appeared that it might be a good alternative to the potassium carbonate due to this.

The governing chemical reactions for the absorption process are as follows:

$$CO_2 + 2RNH_2 + H_2O \rightleftharpoons (RHNH_2)_2CO_3 \qquad (4.2)$$

$$CO_2 + (RHNH_2)_2CO_3 + H_2O \rightleftharpoons 2RHNH_2HCO_3 \qquad (4.3)$$

Where

$R = -CH_2-CH_2OH$ group

RNH_2 = Monoethanolamine

$(RHNH_2)_2CO_3$ = Carbonate

$RHNH_2HCO_3$ = Bicarbonate

The process actually occurs in two steps, with carbonate being formed first. A second reaction then takes place and the carbonate combines with more CO_2 to form a bicarbonate. The bicarbonate leaves the absorber and is run through the pump to the regenerator. The CO_2 is boiled off and monoethanolamine returns through the Pelton wheel and carbonate cooler to the absorber.

The data for monoethanolamine, which was used in the thermodynamic analysis is given in Table 4.1. This data is used with a good deal of confidence in its validity. The heat of reaction and the ratio were taken from the same reference[8] and both are based on calculations and studies

of several workers. The value of the heat of reaction given requires that both reactions, given by Equations 4.2 and 4.3, occur. An equilibrium value of ratio is obtained from two graphs which are a function of temperature, pressure, monoethanolamine concentration and normality. The value of the ratio for the exact conditions desired in this cycle could, therefore, be obtained. The specific volume was obtained from a standard reference[4] and was chosen for a temperature of 176°F (80°C). The specific heat came from a report on monoethanolamine[5].

The efficiency of the plant versus the absorber temperature is plotted in Figure 4.2. The monoethanolamine plant efficiency varies from 14.5% to 15.7%. This is a little less than one half the efficiency of conventional Rankine power cycles and about one third the efficiency calculated for the potassium carbonate. Obviously, monoethanolamine offers no advantage in efficiency over these two cycles.

One advantage in using monoethanolamine is that the mass flow rate, as compared to the potassium carbonate, is much less. Due to its good absorption capacity, only about

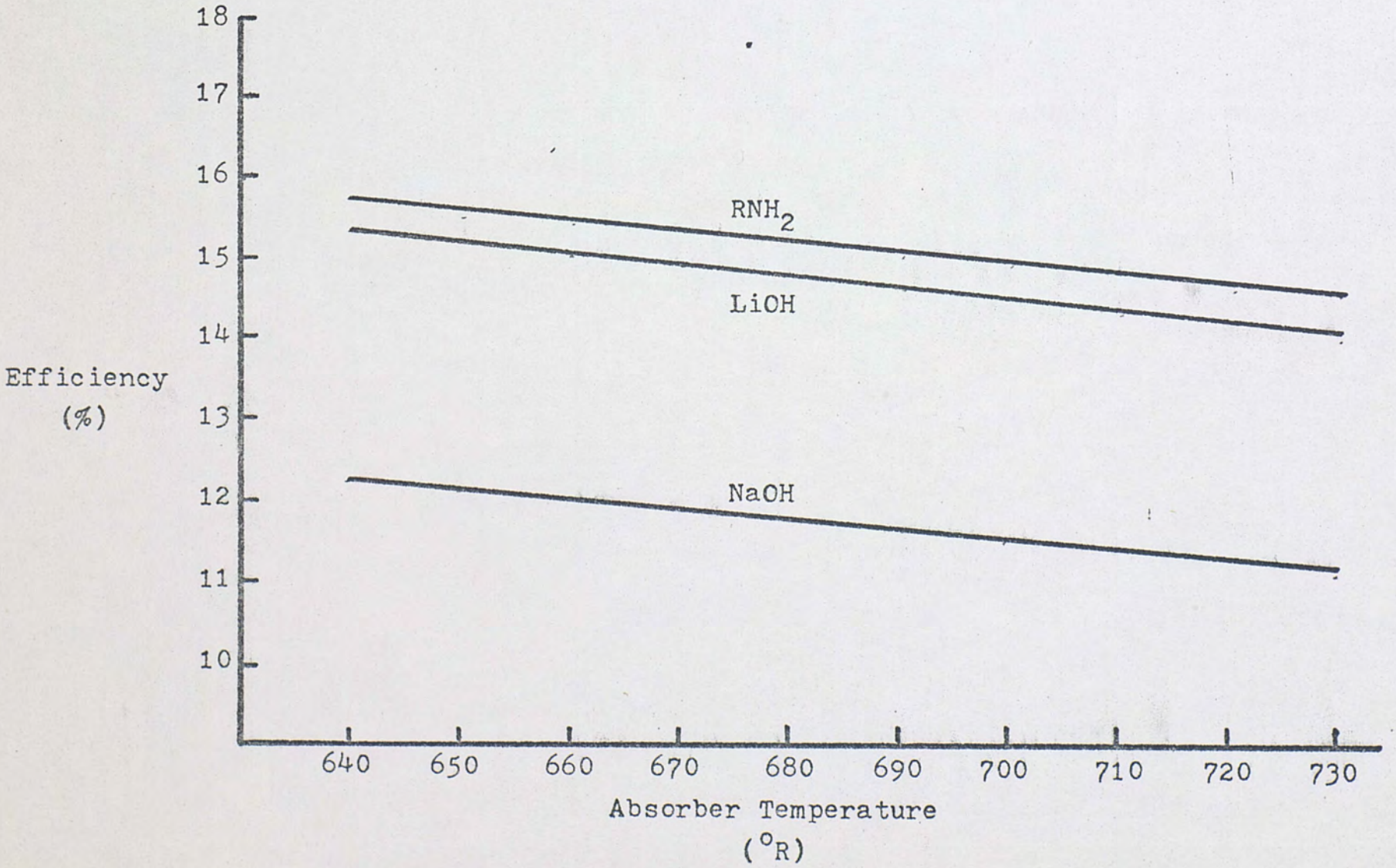

FIGURE 4.2 - CO_2 Cycle Efficiency for RNH_2, NaOH and LiOH

one seventh as much monoethanolamine must be circulated to absorb the same amount of CO_2, as the potassium carbonate. This benefits the cycle in that less net pump work is required. From Equations 3.5 and 3.7, the pump and Pelton wheel work are proportional to the mass flow rates of the carrier fluid and the carrier fluid-CO_2 mixture. The lower the mass flow rate, the less net work that must be done.

A disadvantage of the monoethanolamine solution, other than the low efficiency, is the relatively high heat requirement for regeneration (Table 4.3). It takes approximately two and one half times as much heat to regenerate the monoethanolamine as the potassium carbonate.

4.3.2 Diethanolamine and Triethanolamine

Diethanolamine and triethanolamine are two members of the amine family which are being studied as possible CO_2 absorbers. No numerical results are presented due to the fact that not enough data was available for calculations. The heats of reaction, however, are available[9] and are respectively 653 BTU per pound and 630 BTU per pound, which is nearly as high as monoethanolamine. It can be expected, based solely on the heats of reaction (see Sec-

TABLE 4.3

RESULTS OF CO_2 CYCLE CALCULATIONS, MONOETHANOLAMINE

T_{out} (^{o}R)	640	650	660	670	680
T_{in} (^{o}R)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	1373.9	1270.5	1176.4	1090.7	1012.5
$\dot{m}_{CO2}$ (lb_m/hr)	20598.9	20853.2	21113.9	21381.1	21655.2
R (lb_{car}/lb_{CO2})	2.13	2.13	2.13	2.13	2.13
hor (BTU/lb_m)	828.29	828.29	828.29	828.29	828.29
Q_{abs} (BTU/hr)	17061824.0	17272480.0	17488384.0	17709760.0	17036816.0
W_p (BTU/hr)	293727.6	274542.6	256970.8	240850.0	226036.8
W_{tot} (BTU/hr)	165801.3	154971.9	145052.9	135953.3	127591.7
Q_{cool} (BTU/hr)	408042.9	413080.6	418244.9	423538.3	428968.4
Q_{rs} (BTU/hr)	20715088.0	20941616.0	21172608.0	21408368.0	21649216.0
η_{Carnot}	.562	.555	.548	.541	.534
η_{CO2}	.157	.155	.154	.153	.152

TABLE 4.3 (Continued)

RESULTS OF CO_2 CYCLE CALCULATIONS, MONOETHANOLAMINE

T_{out} (^{o}R)	690	700	710	720	730
T_{in} (^{o}R)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	941.0	875.6	815.7	760.7	710.2
$\dot{m}_{CO_2}$ (lb_m/hr)	21936.5	22225.1	22521.4	22825.8	23138.5
R (lb_{car}/lb_{CO_2})	2.13	2.13	2.13	2.13	2.13
hor (BTU/lb_m)	828.29	828.29	828.29	828.29	828.29
Q_{abs} (BTU/hr)	18169744.0	18408816.0	18654272.0	18906368.0	19165360.0
W_p (BTU/hr)	212403.9	199839.0	188241.6	177522.2	167600.7
W_{tot} (BTU/hr)	119896.3	112803.8	106257.3	100206.5	94606.1
Q_{cool} (BTU/hr)	434539.4	440256.9	446126.9	452155.8	458349.8
Q_{rs} (BTU/hr)	21895408.0	22147296.0	22405152.0	22669328.0	22940112.0
η_{Carnot}	.527	.521	.514	.507	.500
η_{CO_2}	.150	.149	.148	.146	.145

tion 3.7), that the power generation efficiencies would be low, although probably higher than that of monoethanolamine. They are, however, not as effective absorbers as monoethanolamine and have several drawbacks to them.

Although exact figures were not available, it appears, from the literature, that the ratios of diethanolamine and triethanolamine are not as good as monoethanolamine and thus, more carrier fluid must be circulated to absorb the same amount of CO_2, increasing the pump work. They are not as good absorbers of CO_2 as they are other gases, notably, hydrogen sulfide. Triethanolamine, especially, is used for selective absorption of hydrogen sulfide in the presence of large quantities of CO_2. To absorb CO_2, it is used in combination with other chemicals. Triethanolamine is also unstable and is used in combination with sodium carbonate for low temperature absorption (40-50°F)[10].

These two fluids do not look as favorable as potassium carbonate but due to lack of data, further study would be necessary to validate this conclusion.

4.4 Lithium Hydroxide

Lithium hydroxide has a heat of reaction approximately equal to that of monoethanolamine. However, it has a ratio of pounds of carrier fluid to pounds of CO_2 absorbed about half that of the monoethanolamine. This implies that about half as much lithium hydroxide must be circulated to absorb the same amount of CO_2. Due to the heat of reaction, it was expected that the efficiency would be about the same as that of monoethanolamine. However, it was expected that the pump work would be lower due to the low ratio and necessary mass flow.

The governing chemical reactions for the absorption of CO_2 by lithium hydroxide are:

$$2LiOH + 2H_2O \rightleftharpoons 2LiOH \cdot H_2O \qquad (4.4)$$

$$2LiOH \cdot H_2O \rightleftharpoons Li_2CO_3 + 3H_2O \qquad (4.5)$$

The chemical reaction occurs in two steps, but it is the second step that is concerned with CO_2 absorption. The first step is concerned with the mixing of lithium hydroxide and water to form a solution. The two combine to form lithium hydroxide monohydrate, $LiOH \cdot H_2O$, which combines well with CO_2.

The data used for lithium hydroxide is presented in Table 4.1. The value of the heat of reaction requires that both reactions, given by Equations 4.4 and 4.5, occur. Therefore, in the regenerator, the solution must completely decompose to lithium hydroxide, water and CO_2. The CO_2 is piped to the superheater, while the lithium hydroxide and water recirculate to the absorber. There, they recombine to produce the amount of heat given in Table 4.1.

The validity of the data for lithium hydroxide is a question. The absorption rate of CO_2 by lithium hydroxide and the heat of reaction are based on absorption of CO_2 by a mixture of water and lithium hydroxide granules in a chamber through which CO_2 gas is passed[11]. For the CO_2 cycle, the carrier must be in a form that can be piped and pumped. The validity of applying the above data to a liquid form is questionable. Indeed, the idea that the mixture decomposes in the regenerator to LiOH and water, is also doubtful. It is assumed, however, for this process, that the above are applicable or that a fluid exists that has the approximate above characteristics and can be used in this cycle. In any case, lithium hydroxide could be considered as a fluid to verify the effect of the heat of reaction on the efficiency. The

TABLE 4.4

RESULTS OF CO_2 CYCLE CALCULATIONS, LITHIUM HYDROXIDE

T_{out} (^oR)	640	650	660	670	680
T_{in} (^oR)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	1373.9	1270.4	1176.4	1090.7	1012.5
$\dot{m}_{CO_2}$ (lb_m/hr)	20598.9	20853.1	21113.9	21381.1	21655.2
R (lb_{car}/lb_{CO_2})	1.25	1.25	1.25	1.25	1.25
hor (BTU/lb_m)	876.22	876.22	876.22	876.22	876.22
Q_{abs} (BTU/hr)	18049136.0	18271968.0	18500384.0	18734560.0	18974752.0
W_p (BTU/hr)	158648.8	148286.7	138795.8	130088.4	122087.5
W_{tot} (BTU/hr)	102240.3	95562.5	89446.1	83834.7	78678.6
Q_{cool} (BTU/hr)	247186.4	250238.3	253366.3	256573.3	259862.8
Q_{rs} (BTU/hr)	21605104.0	21837648.0	22075312.0	22318304.0	22566944.0
η_{Carnot}	.562	.555	.548	.541	.534
η_{CO_2}	.153	.152	.150	.149	.148

TABLE 4.4 (Continued)

RESULTS OF CO_2 CYCLE CALCULATIONS, LITHIUM HYDROXIDE

T_{out} (^{o}R)	690	700	710	720	730
T_{in} (^{o}R)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	941.0	875.6	815.7	760.7	710.2
$\dot{m}_{CO_2}$ (lb_m/hr)	21936.5	22225.1	22521.4	22825.8	23138.5
R (lb_{car}/lb_{CO_2})	1.25	1.25	1.25	1.25	1.25
hor (BTU/lb_m)	876.22	876.22	876.22	876.22	876.22
Q_{abs} (BTU/hr)	19221168.0	19474080.0	19733728.0	20000400.0	20274384.0
W_p (BTU/hr)	114724.1	107937.4	101673.5	95883.7	90524.9
W_{tot} (BTU/hr)	73933.3	69559.6	65522.9	61791.7	58338.2
Q_{cool} (BTU/hr)	263237.6	266701.3	270257.2	273909.4	277661.6
Q_{rs} (BTU/hr)	22821472.0	23082224.0	23349472.0	23623520.0	23904704.0
η_{Carnot}	.527	.521	.514	.507	.500
η_{CO_2}	.146	.145	.143	.142	.140

specific volume and the specific heat were taken from reference 4 at a temperature of 176°F (80°C).

From Figure 4.2, lithium hydroxide has an efficiency approximately the same as monoethanolamine. This is expected since the heats of reaction are nearly equal.

4.5 Sodium Hydroxide

Sodium hydroxide was considered as a carrier fluid chiefly due to its heat of reaction, which is above that of the other three. It became apparent, that the heat of reaction was the one factor which had the most control over the cycle efficiency. Calculations for sodium hydroxide were performed to verify this effect.

The governing chemical reactions for the absorption of CO_2 by sodium hydroxide are:

$$2NaOH + H_2O + CO_2 \rightleftharpoons Na_2CO_3 + 3H_2O \qquad (4.6)$$

$$Na_2CO_3 + H_2O + CO_2 \rightleftharpoons 2NaHCO_3 \qquad (4.7)$$

The carbonate, Na_2CO_3, is first formed, but it quickly combines with more water and CO_2 to form the bicarbonate, $NaHCO_3$. The bicarbonate is the fluid that leaves the

absorber and proceeds to the regenerator where the reactions take place in reverse.

The data used for sodium hydroxide is given in Table 4.1. It is more reliable than that of lithium hydroxide but it is not as reliable as monoethanolamine. The heat of reaction and the ratio were obtained from the same reference[8]. However, while the ratio was given for sodium hydroxide, the heat of reaction was given for the general class of alkali hydroxides. It can, therefore, be used only as a rough estimate of the heat of reaction of sodium hydroxide. The ratio, on the other hand, while valid for sodium hydroxide exclusively, is a theoretical value based on the chemical reaction. Generally, the carrier fluid cannot absorb the amount of CO_2 calculated from theoretical considerations. Therefore, the practical value of ratio would not be as low as the theoretical value. Recognizing that the theoretical value also does not take into account the temperature and pressure effects, the practical value could be much different from that used in this study. The The specific heat and specific volume were taken from references 4 and 7 at a temperature of 176°F (80°C) and can be assumed to be valid.

Examining Figure 4.2, sodium hydroxide has a power generation efficiency lower than that of monoethanolamine and lithium hydroxide and substantially lower than potassium carbonate. Comparing the heats of reaction and the efficiencies of all four fluids, as the heat of reaction increases, the power generation efficiency decreases. Conversely, a lower heat of reaction is associated with a higher efficiency. This partially verifies Equation 3.30. Equation 3.30 also says that the efficiency is inversely proportional to the heat release from the carbonate cooler. However, due to the magnitudes of the quantities and the relative changes between them, the heat of reaction has a greater effect on the efficiency than the heat release from the carbonate cooler. While the ratio and nass flow rate are also important in determining the efficiency, knowledge of the heat of reaction will provide an estimate to the range of the efficiency before calculations are performed.

4.6 Results

Examining the graphs and tables for the carrier fluids, it is obvious that potassium carbonate affords the best efficiency. It also yields a better efficiency than the conventional Rankine cycle.

TABLE 4.5

RESULTS OF CO_2 CYCLE CALCULATIONS, SODIUM HYDROXIDE

T_{out} (^{o}R)	640	650	660	670	680
T_{in} (^{o}R)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	1373.9	1270.5	1176.4	1090.7	1012.5
$\dot{m}_{CO_2}$ (lb_m/hr)	20598.9	20853.2	21113.9	21381.1	21655.2
R (lb_{car}/lb_{CO_2})	.909	.909	.909	.909	.909
hor (BTU/lb_m)	1146.85	1146.85	1146.85	1146.85	1146.85
Q_{abs} (BTU/hr)	23623808.0	23915472.0	24214416.0	24520928.0	24835296.0
W_p (BTU/hr)	148477.9	138780.1	129897.6	121748.5	114260.5
W_{tot} (BTU/hr)	103227.3	96485.0	90309.6	84644.0	79438.1
Q_{cool} (BTU/hr)	174158.8	176305.9	178509.8	180769.4	183087.0
Q_{rs} (BTU/hr)	27105144.0	27466304.0	27713616.0	28028064.0	28349936.0
η_{Carnot}	.562	.555	.548	.541	.534
η_{CO_2}	.122	.121	.120	.119	.118

TABLE 4.5 (Continued)

RESULTS OF CO_2 CYCLE CALCULATIONS, SODIUM HYDROXIDE

T_{out} (^{o}R)	690	700	710	720	730
T_{in} (^{o}R)	1460	1460	1460	1460	1460
P_{out} (psia)	25	25	25	25	25
P_{in} (psia)	941.0	875.6	815.7	760.7	710.2
$\dot{m}_{CO2}$ (lb_m/hr)	21936.5	22225.1	22521.4	22825.8	23138.5
R (lb_{car}/lb_{CO_2})	.909	.909	.909	.909	.909
hor (BTU/lb_m)	1146.85	1146.85	1146.85	1146.85	1146.85
Q_{abs} (BTU/hr)	25157840.0	25488848.0	25828704.0	26177744.0	26536352.0
W_p (BTU/hr)	107369.2	101017.6	95155.3	89736.6	84721.3
W_{tot} (BTU/hr)	74646.9	70231.1	66155.4	62388.2	58901.4
Q_{cool} (BTU/hr)	185464.8	187905.0	190410.4	192983.5	195627.0
Q_{rs} (BTU/hr)	28679664.0	29017536.0	29363952.0	29719344.0	30084080.0
η_{Carnot}	.527	.521	.514	.507	.500
η_{CO_2}	.116	.115	.114	.113	.111

These four fluids are not the only fluids that could be used in this cycle. There are many commercially available absorbents that could be used, with possibly better results. Similarly, CO_2 is not the only gas that could be used in this cycle. Some other gas, or other combination of carrier fluid and gas, might produce better efficiencies.

In examing other carrier fluids, it is possible to obtain an idea about the performance by examining the data. The efficiency is inversely proportional to the heat of reaction which is the main factor in determining its value. The ratio is proportional to the mass flow rate and is the main determining factor in the amount of pump work. Generally, without performing calculations, the best carrier fluids, efficiency-wise, will be those with a low heat of reaction and a high absorption capacity (low ratio).

CHAPTER 5

BINARY ASPECT FOR DESALINATION

5.1 Introduction

Coupled with the energy crisis is the increasing rate at which pure water is being consumed. About 1100 billion gallons of water is available, per day, in the United States as runoff[12] although the cost to catch all of it would be prohibitive. This is the theoretical upper limit of the water supply. In 1954, the demand amounted to about 300 billion gallons per day or about 27% of the available supply. By the year 2000, this demand is expected to be 900 billion gallons per day or about 82% of the available supply. By the year 2000, the water crisis could become more serious than the energy crisis.

It is ironic, that there is an inexhaustible supply of water, readily available, that is unfit to drink. This is the oceans, which account for 97% of the worlds water. This water can be made fit to drink, however, by desalination, thereby taking some of the burden off the natural fresh water supply.

The binary CO_2 cycle can be coupled with a desalination plant to produce fresh water, while maintaining a higher power generation efficiency than that of conventional Rankine cycles. The desalination plant makes use of the waste heat, generated by the absorber and carbonate cooler, to heat sea water for multistage flash distillation. The CO_2 cycle can generate power at high efficiencies, even with the high turbine outlet temperature required to accomodate the desalination process.

5.2 Desalting Techniques

5.2.1 Introduction

There are many desalting processes presently in use and several were studied to determine the best to combine with the CO_2 cycle. Only the cycles which utilize heat as the energy source were considered. A few of the most popular are presented here.

5.2.2 Long Tube Vertical Distillation

Raw sea water falls through long metal tubes located inside a chamber filled with steam (Figure 5.1). The exchange of heat vaporizes some of the cold water in the pipe and at the same time condenses some of the

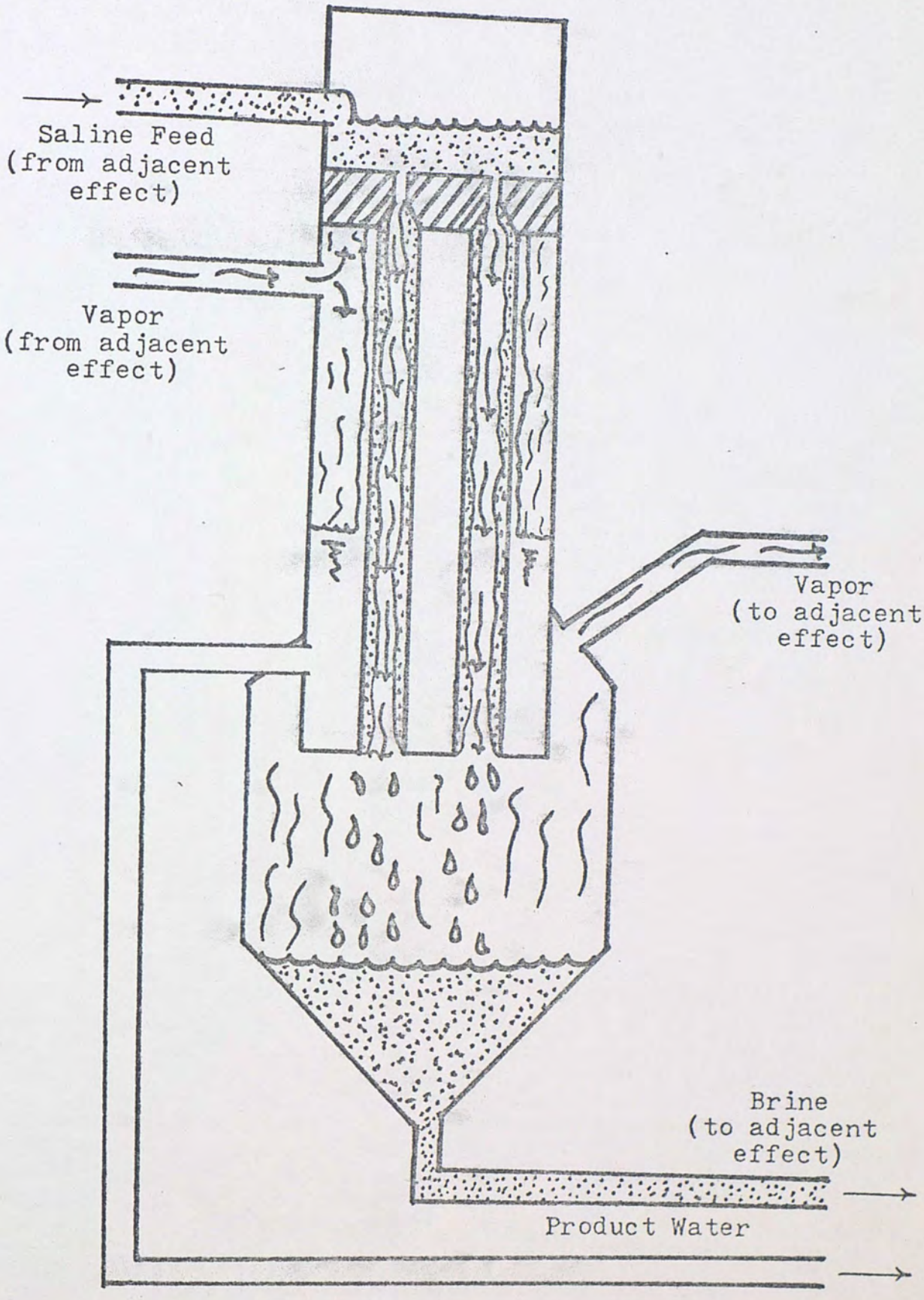

FIGURE 5.1 - Long Tube Vertical Distillation

steam on the outside of the pipe. This is the product water which is collected and stored. The vaporized sea water in the pipe becomes the steam for the next stage (steam for the first stage is supplied from an outside source) which is maintained at a slightly lower pressure allowing the steam to condense at a lower temperature. The unvaporized sea water is piped to the next stage where it falls through another bundle of tubes. This process is repeated in several stages.

This is a very popular technique, and is presently used quite extensively. It, however, is not as efficient as the multistage flash distillation plant and is not recommended that it be used in conjunction with the CO_2 cycle.

5.2.3 Vapor Compression Distillation

Raw sea water is pumped into an evaporation chamber which initially, is heated by an outside source of heat (Figure 5.2). Some of the sea water evaporates and is drawn off. The vapor is compressed by a pump, thus raising its temperature. This hot steam, which is the product fresh water, is then cycled back to the evaporation chamber through coils and is cooled off by giving up its heat to

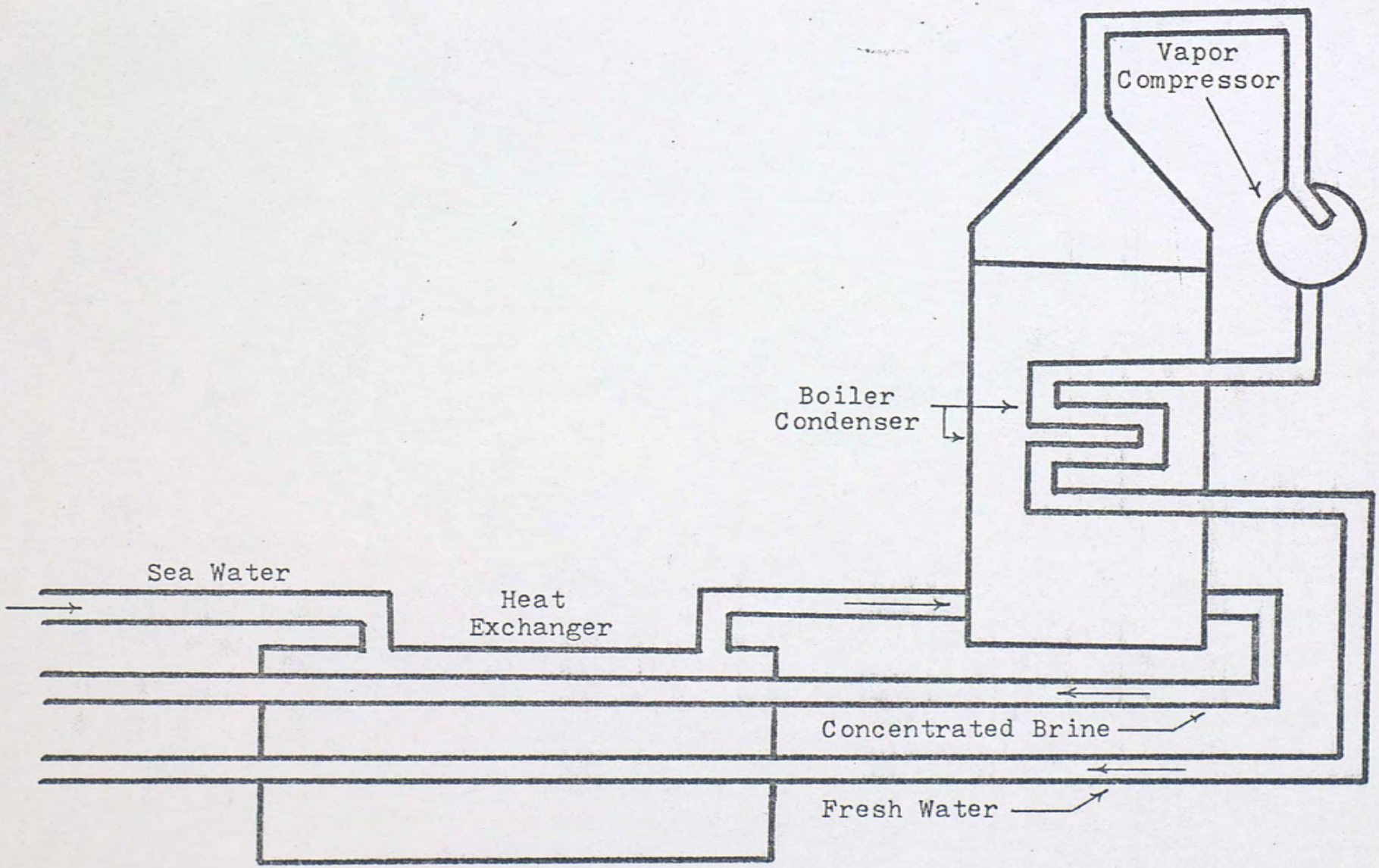

FIGURE 5.2 - Vapor Compression Distillation Plant

the sea water in the evaporation chamber. Enough heat is generated by the pump in compressing the vapor to heat the sea water. Thus once the cycle is established, the external source of heat may be removed. Thereafter, the energy supplied to the cycle must be in the form of pump work.

It is obvious that this process is not compatable with the CO_2 cycle. The heat supplied by the absorber and carbonate cooler could be used to start up the plant, but once in operation, pump work, rather than heat, is needed to keep the desalting process going.

5.3 Multistage Flash Distillation

The multistage flash distillation process is the most developed and most widely used of the desalting processes. It can make use of the waste heat generated by the absorber and carbonate cooler and do it most efficiently. The process discussed here is shown in Figure 5.3.

From the boiler, heated sea water enters the first of a series of "flash" chambers. The chamber is maintained at a pressure just below the equilibrium vapor pressure for the temperature at which the sea water is entering.

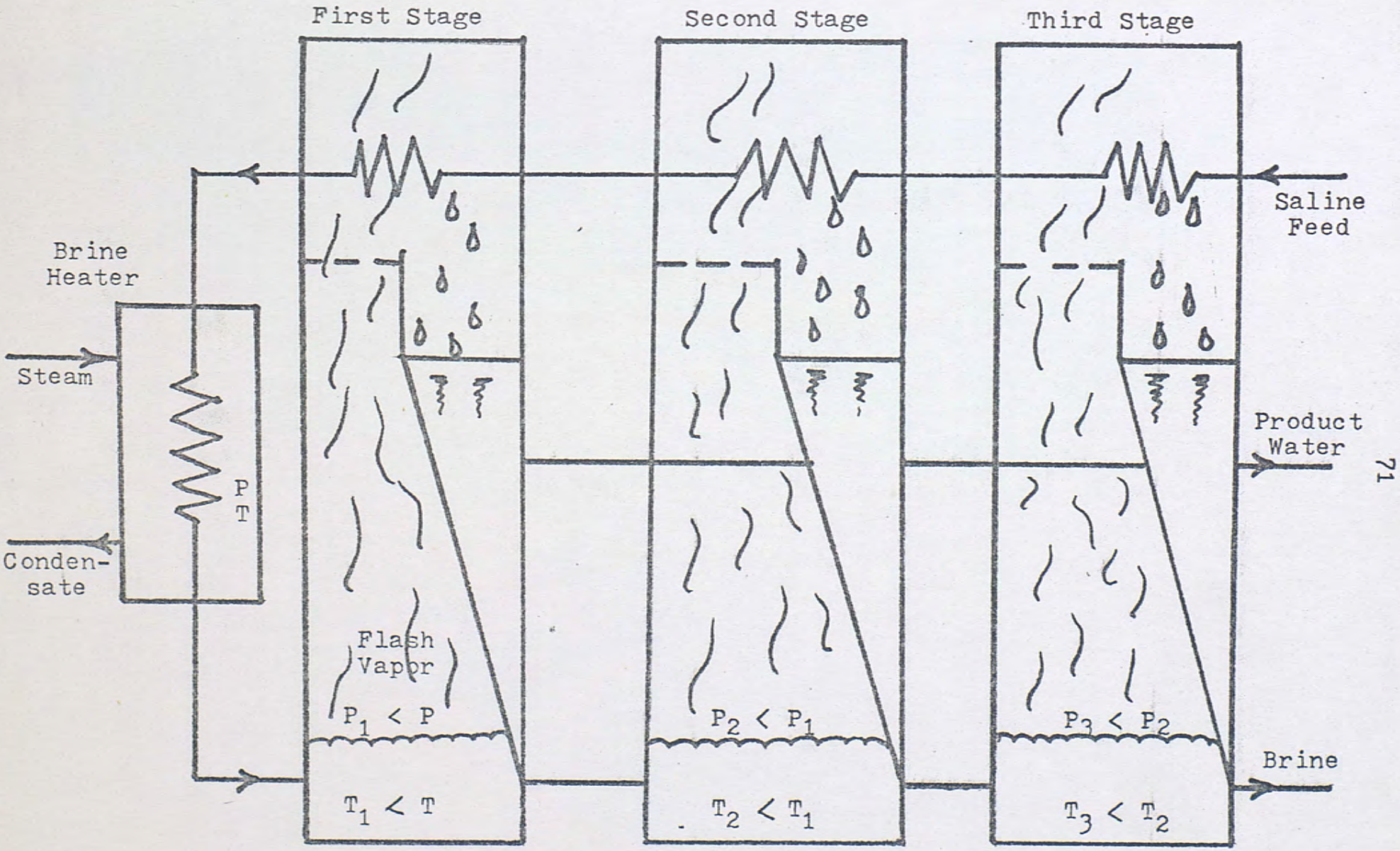

FIGURE 5.3 - Multistage Flash Distillation Plant

In other words, the entering sea water is at a higher temperature than the boiling temperature for the pressure at which the chamber is maintained. Therefore, upon entering the chamber, some of the sea water is immediately "flashed" or boiled into vapor, leaving the impurities behind in the liquid (brine). This vapor is the salt free product water which condenses on cooling coils at the top of the chamber and is collected. The brine cools cown, due to the fact it is losing latent heat required by the vaporization, until the temperature drops below the boiling point and the flashing stops. The brine moves to another chamber, where the temperature and pressure are lower, and the process begins again.

The raw sea water entering the plant is used as the coolant in the cooling coils. The vapor produced in each chamber condenses on the coil, giving up its latent heat to the sea water coolant, thereby preheating it before it arrives at the boiler. The coolant sea water enters the plant by way of the last stage and proceeds progressively through the plant, finally exiting through the first stage. In this way, it is progressively raised in temperature until at exit from the cooling coils, at the top of the first

stage, the preheated sea water is within 15-30 degrees of its final temperature at the boiler exit. The boiler heats it the last few degrees to the desired temperature.

The multistage flash distillation process uses the heat added to the sea water more efficiently than the other distillation processes because 90% of the heat acquired by the sea water is obtained in the cooling coils by the colder sea water as it moves through each chamber. In other words, if one cycle is considered, 90% of the heat added in that cycle would be reused in heating up more sea water in the next cycle (through the cooling coils). Only 10% of the heat needed in a cycle would be "new" heat added by the boiler. This cannot be matched by any other distillation process.

The multistage flash distillation process is the best process to use in conjunction with the CO_2 cycle. It can make use of the waste heat generated by the cycle and do it most efficiently.

5.4 Thermodynamic Analysis

If a single chamber is isolated (Figure 5.4), the equations necessary for calculating the amount of fresh water pro-

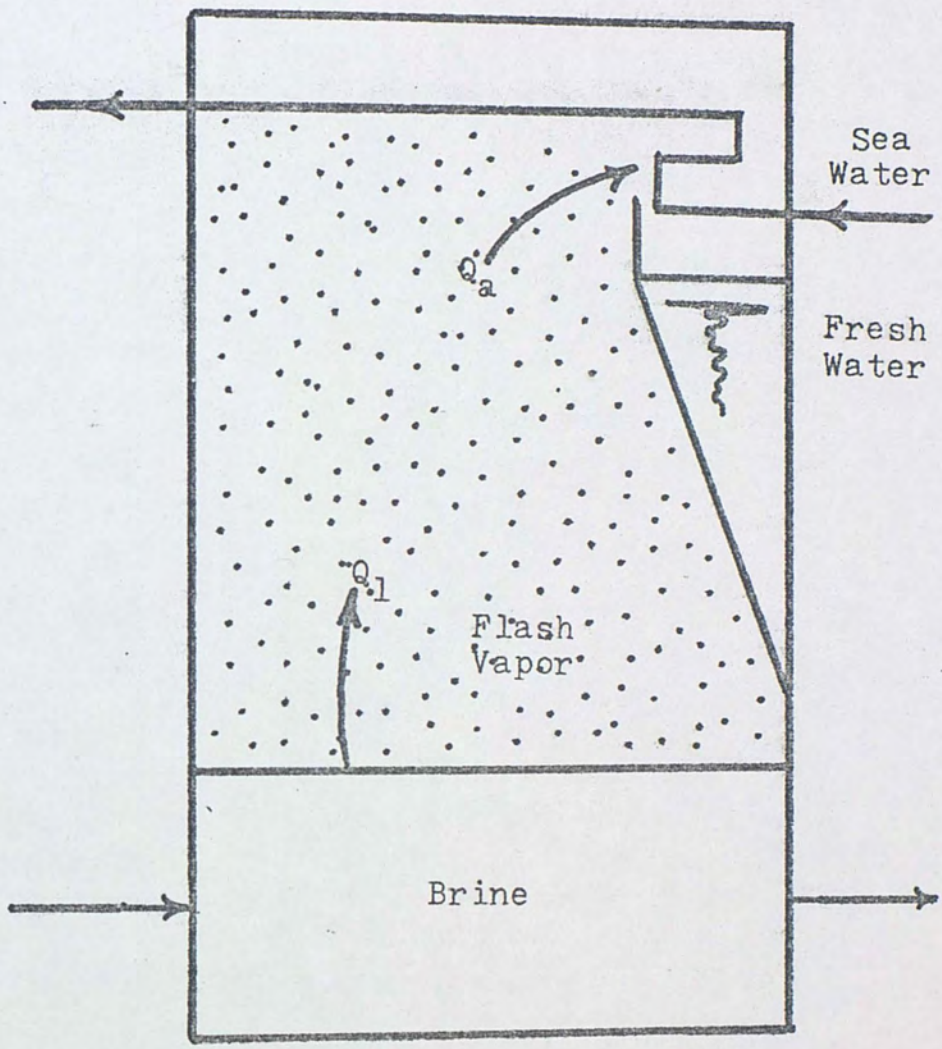

FIGURE 5.4 - Multistage Flash Distillation Plant, Single Chamber

duced by flash distillation can be derived. The result of the following development will verify an equation from reference 13 that was presented without derivation.

When the liquid sea water flashes to vapor, it must give up its latent heat to the vapor. The total amount of heat acquired by the vapor, per unit time, is simply the latent heat times the rate of vapor production. That is:

$$Q_a = M\lambda \qquad (5.1)$$

Where Q_a = Amount of heat transfered to the vapor per unit time

M = Rate of vapor production

λ = Latent heat

The amount of heat lost by the liquid per unit time is the difference in the enthalpies before and after flashing times the mass flow rate of the brine. That is:

$$Q_l = \omega \Delta h \qquad (5.2)$$

Where Q_l = Amount of heat lost by the liquid per unit time

ω = Brine mass flow rate

Δh = Enthalpy difference before and after flashing

The total amount of heat transfered for all the stages is simply the sum of the heat transfers for each stage:

$$\sum_{i=1}^{n} Q_{a_i} = M_1\lambda + M_2\lambda + \ldots + M_n\lambda \qquad (5.3)$$

and,

$$\sum_{i=1}^{n} Q_{l_i} = \omega_1\Delta h_1 + \omega_2\Delta h_2 + \ldots + \omega_n\Delta h_n \qquad (5.4)$$

The subscripts denote the different stages and n is the number of stages.

λ can be factored out of the right side of Equation 5.3 and the vapor produced for each stage added to get the total amount of vapor (fresh water) produced:

$$\sum_{i=1}^{n} Q_{a_i} = M_1\lambda + M_2\lambda + \ldots + M_n\lambda = M_{tot}\lambda \qquad (5.5)$$

Where M_{tot} = Total amount of fresh water produced

The amount of vapor flashed in a stage is small compared with the amount of sea water being circulated and it can be assumed that the amount of sea water circulated in each stage, remains the same. In other words:

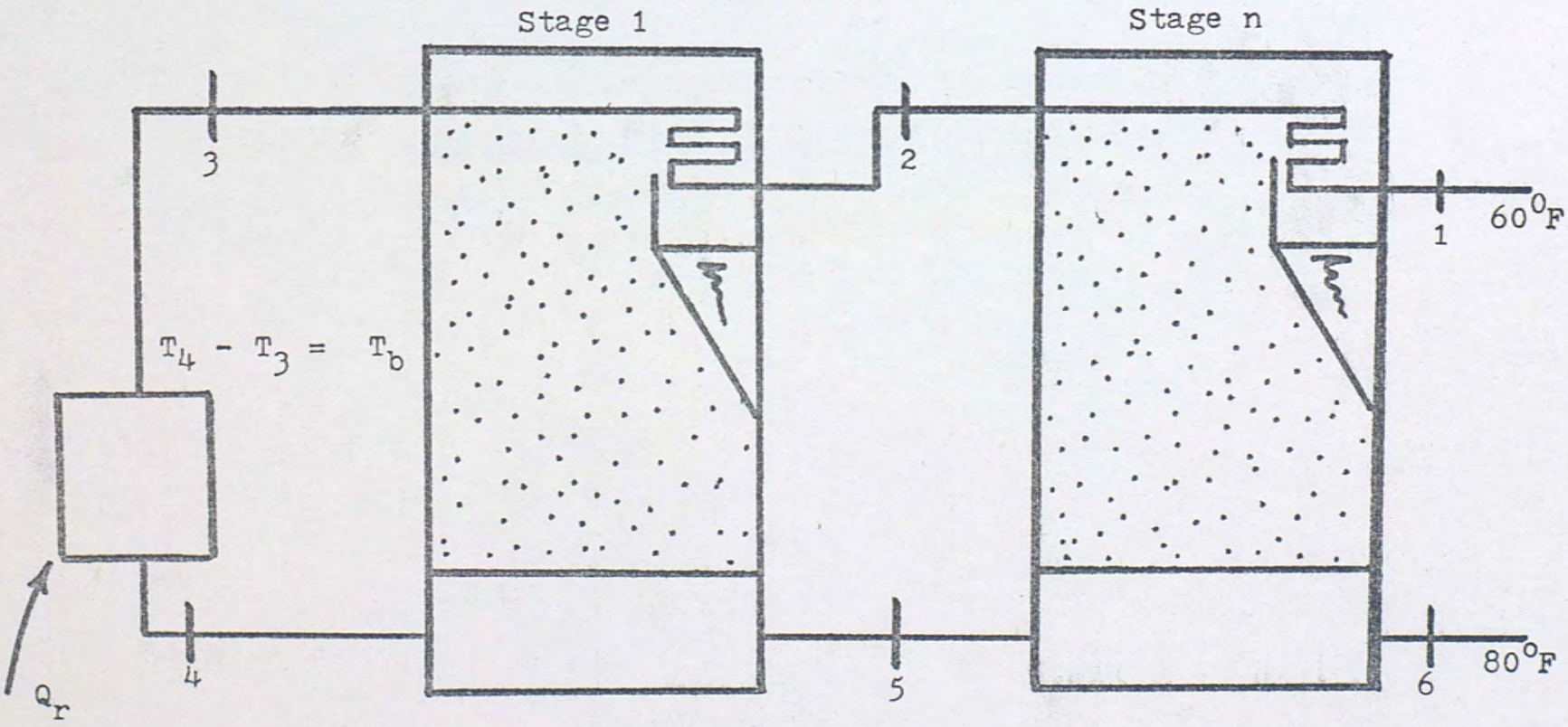

FIGURE 5.5 - Multistage Flash Distillation Plant,
First and nth stage

$$\omega_1 \approx \omega_2 \approx \cdots \approx \omega_n = \omega \qquad (5.6)$$

Where ω will now be the amount of sea water circulated. In practice, $\omega_n \approx .9\omega_1$[12].

The total enthalpy difference is the sum of the enthalpy differences for the individual stages. Neglecting losses, the enthalpy of the sea water leaving one stage is equal to the enthalpy of the sea water entering the next stage. The total enthalpy difference across all the stages, therefore, is simply the difference in enthalpies of the sea water entering the first stage and the sea water leaving the last stage. As an illustration, consider Figure 5.5 and assume the plant consists of only two stages, stage 1 and stage n. From Equation 5.4:

$$\sum_{i=1}^{n} Q_{l_i} = \omega_1 \Delta h_1 + \omega_n \Delta h_n \qquad (5.7)$$

From Figure 5.5:

$$\Delta h_1 = h_5 - h_4 \; ; \; \Delta h_n = h_6 - h_5 \qquad (5.8)$$

Substituting Equations 5.6 and 5.8 into Equation 5.7:

$$\sum_{i=1}^{n} Q_{l_i} = \omega[(h_5 - h_4) + (h_6 - h_5)] \qquad (5.9)$$

Simplifying:

$$\sum_{i=1}^{n} Q_{l_i} = \omega(h_6 - h_4) = \omega \Delta h_{1,n} \qquad (5.10)$$

Where $\Delta h_{1,n}$ = Total enthalpy difference across both stages

h_6 = Enthalpy of sea water leaving last stage

h_4 = Enthalpy of sea water entering first stage

Application of the same analysis to any number of stages will give:

$$\sum_{i=1}^{n} Q_{l_i} = \omega \Delta h_{tot} \qquad (5.11)$$

Where Δh_{tot} = Total enthalpy difference across all n stages or the enthalpy at exit from the last stage minus the enthalpy at entrance to the first stage

Examining the whole cycle (Figure 5.6), a heat balance can be derived to determine the amount of fresh water produced. The temperatures shown in Figure 5.6 are typical of conventional multistage flash distillation plants and will be used as the basis for this analysis.

For a heat balance, the sea water is considered a system, and the heat acquired by the sea water going into the plant must equal the heat lost by the sea water coming out of the plant. The heat acquired by the sea water is the heat picked up in the cooling coils in each stage, Q_a, given by Equation 5.1, and the heat acquired in the boiler, Q_r. The heat lost by the sea water is the enthalpy difference of the sea water across each stage given by Q_l and Equation 5.2. For the process to be considered a complete cycle for which a heat balance can be written, the sea water must leave the plant at the same condition (i.e. temperature) at which it entered. As in Figure 5.6, the exit temperature is typically 20° higher than the entrance temperature. Since this energy at the exit is never used by the cycle (i.e. the temperature is not dropped to $60^{\circ}F$ as at the entrance), it must be considered a loss and added to Q_l. The loss can be accounted for by the enthalpy difference of sea water at $80^{\circ}F$ and $60^{\circ}F$. In other words:

$$Q_{l_e} = \omega_e(h_{80} - h_{60}) \qquad (5.12)$$

Where Q_{l_e} = Heat loss due to unused energy at the exit

ω_e = Sea water flow rate at exit

h_{80} = Enthalpy of sea water at $80^{o}F$

h_{60} = Enthalpy of sea water at $60^{o}F$

A cyclic process is thereby obtained and an energy balance can be written as:

$$\sum_{i=1}^{n} Q_{a_i} + Q_r = \sum_{i=1}^{n} Q_{l_i} + Q_{l_e} \qquad (5.13)$$

Where Q_r = Heat from the CO_2 cycle used for heating the sea water

Substituting Equations 5.5, 5.11 and 5.12 into Equation 5.13 for Q_a, Q_l and Q_{l_e}:

$$M_{tot}\lambda + Q_r = \omega\Delta h_{tot} + \omega_e(h_{80} - h_{60}) \qquad (5.14)$$

Δh_{tot} and $h_{80} - h_{60}$ can be approximated by $c_p\Delta T$ (See Appendix A.1), where c_p is the specific heat at constant pressure and T is the temperature difference. Therefore:

$$\Delta h_{tot} = c_p\Delta T_{tot} \qquad (5.15)$$

Where ΔT_{tot} = Temperature difference between entrance to first stage and exit to last stage

Similarly:

$$h_{80} - h_{60} = c_p(80 - 60) = 20c_p \qquad (5.16)$$

Substituting Equations 5.15 and 5.16 into Equation 5.14 and recognizing that by Equation 5.6, $\omega_e = \omega$:

$$M_{tot}\lambda + Q_r = c_p\Delta T_{tot} + c_p(20) \qquad (5.17)$$

Equation 5.17 can be used to find the amount of fresh water, M_{tot}, produced by a conventional multistage flash distillation plant.

Close examination of Equation 5.17 reveals, however, there is a second unknown, other than M_{tot}. The specific heat and latent heat of vaporization are known constants and the temperature difference across the stages is specified. Q_r is a fixed quantity of heat generated by the exothermic reaction in the CO_2 cycle, plus the heat released by the carbonate cooler, and is thus a known value. The sea water circulation, ω, however, is generally unknown and cannot be specified. A second equation must be derived to allow a solution to Equation 5.17.

For a boiler, where $\Delta P = W = 0$, the following relation is obtained (See Appendix A.5):

$$\dot{m}\Delta h = Q \qquad (5.18)$$

Where $\dot{m}$ = Mass flow rate of the liquid in the boiler

Δh = Enthalpy change of the liquid passing through the boiler

Q = Heat added to the boiler

As before, Δh can be approximated by $c_p \Delta T$, therefore:

$$\dot{m} c_p \Delta T = Q \qquad (5.19)$$

Applying this relation to the boiler in the multistage flash distillation plant:

$$c_p \Delta T_b = Q_r \qquad (5.20)$$

Where ΔT_b = Temperature difference across the boiler

Rearranging Equation 5.20:

$$\omega = \frac{Q_r}{c_p \Delta T_b} \qquad (5.21)$$

Equation 5.21 can be used to determine the mass flow rate of sea water that must be circulated to generate the amount of fresh water given by Equation 5.17. Equation 5.21 can be substituted into Equation 5.17 to yield one expression for determining the amount of fresh water pro-

duced:

$$M_{tot}\lambda + Q_r = \frac{Q_r c_p \Delta T_{tot}}{c_p \Delta T_b} + \frac{Q_r c_p 20}{c_p \Delta T_b} \qquad (5.22)$$

Combining terms and solving for M_{tot}:

$$M_{tot} = \frac{Q_r}{\lambda}\left(\frac{\Delta T_{tot} + 20}{\Delta T_b} - 1\right) \qquad (5.23)$$

Using Figure 5.6, however, a simpler equation can be found to determine the amount of fresh water produced. Neglecting losses, the heat lost by the liquid sea water has to equal the heat gained by the vapor. In other words:

$$Q_a = Q_l \qquad (5.24)$$

For n stages:

$$\sum_{i=1}^{n} Q_{a_i} = \sum_{i=1}^{n} Q_{l_i} \qquad (5.25)$$

Substituting Equations 5.5 and 5.11 into Equation 5.25 and using $\Delta h = c_p \Delta T$:

$$M_{tot}\lambda = \omega c_p \Delta T_{tot} \qquad (5.26)$$

Equation 5.26 can be used in place of Equation 5.17 to determine the amount of fresh water produced. Once again

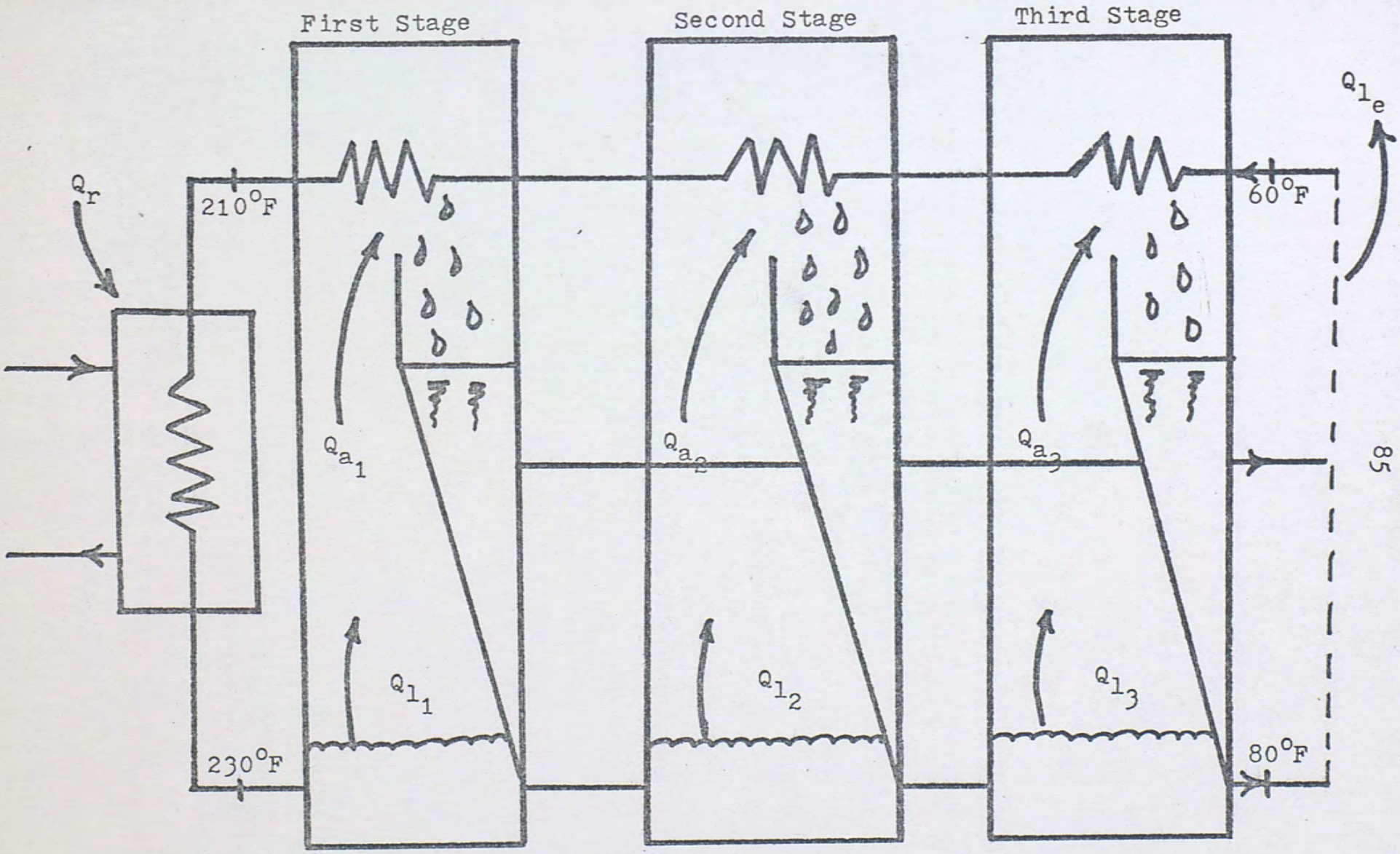

FIGURE 5.6 - Multistage Flash Distillation Plant
Showing Heat Balances and Temperatures

ω is an unknown and must be solved for by the use of Equation 5.21. If Equation 5.21 is substituted into Equation 5.26, a very simple relation for the amount of fresh water produced results:

$$M_{tot}\lambda = \frac{Q_r \Delta T_{tot}}{\Delta T_b} \qquad (5.27)$$

Solving for M_{tot}:

$$M_{tot} = \frac{Q_r \Delta T_{tot}}{\lambda \Delta T_b} \qquad (5.28)$$

Equation 5.28 (in the form of Equation 5.26) verifies the equation presented in reference 13.

An interesting design point is made apparent by manipulation of Equations 5.17 and 5.26. Subtracting the equal quantities of Equation 5.26 from each side of Equation 5.17:

$$Q_r = \omega c_p 20 \qquad (5.29)$$

Equation 5.29 implies that the heat added to the boiler, from the CO_2 cycle, is equal to the heat lost at the end of the desalination cycle.

Neglecting losses the heat, Q_r, added to the boiler will

be realized by the enthalpy change of the sea water passing through the boiler (in the same manner as Equation 5.18):

$$Q_r = \omega_b \Delta h_b \qquad (5.30)$$

Where ω_b = Sea water circulation through the boiler

Δh_b = Enthalpy change of the sea water in passing through the boiler

As before, Δh can be approximated by $c_p \Delta T$ or in this case, $c_p \Delta T_b$:

$$Q_r = \omega_b c_p \Delta T_b \qquad (5.31)$$

Substituting Equation 5.31 into Equation 5.29:

$$\omega_b c_p \Delta T_b = \omega c_p 20 \qquad (5.32)$$

It was assumed that the sea water circulation would remain approximately the same throughout the cycle, therefore:

$$\omega_b = \omega \qquad (5.33)$$

The specific heat of sea water is also assumed to remain constant. Dividing both sides of Equation 5.32 by ωc_p:

$$\Delta T_b = 20 \qquad (5.34)$$

In more general terms, the temperature difference across the boiler is the same as the temperature difference of the sea water entering the first stage, going into the plant as cooling water, and leaving the last stage, coming out of the plant as brine. This occurs in practice[14]. However, there might be a slight difference in values due to losses or other considerations not mentioned here.

Equation 5.23 is a more general equation than Equation 5.28. Equation 5.28 involves the assumption that there are no losses and the acquired heat of the flash vapor is equal to the enthalpy difference of the circulating sea water. This, in turn, requires that the boiler temperature difference must equal the temperature difference of the rejected brine and the input raw sea water. Equation 5.28, however, does not involve this assumption and thus, the boiler temperature difference does not depend on the temperatures of the exit brine or the raw inlet sea water. Depending on the efficiency of the heat transfer between the sea water and the flash vapor, the boiler temperature difference can vary substantially. Ideally, Equation 5.28 is desired. (Equation 5.28 can be obtained from Equation

5.23 by letting $\Delta T_b = 20^o$.)

It should be noted, that the absorber and carbonate cooler control the boiler exit temperature. It is assumed that the heat generated in the absorber and the carbonate cooler is at the same temperature as the fluid in the two devices. Since the boiler acquires its heat from these two devices, assuming no losses, the boiler exit temperature will be the same as the absorber and carbonate cooler temperatures.

It should also be noted that Equations 5.23 and 5.28 are derived under steady state operating conditions and would not be valid at plant startup. However, multistage flash distillation plants are run continuously (except for infrequent periodic maintenance) and the important condition for which the amount of water production is desired is the steady state operating condition.

Finally, it should be understood that the process and calculations made here are a very simplified representation of the actual process. In actuality, there are many different water circulations and heat transfers taking place, although their effects are small. There is, however, one

water circulation not considered in this analysis, that is present in the actual process, which could have a significant effect on the fresh water production. In the actual process, 10% of the sea water is converted to fresh water in one cycle. Another 10% is removed after the last stage to control the salinity of the brine. Eighty per cent of the brine, however, is recirculated through the cycle with enough raw sea water added to make up for the amount lost. The recirculated brine is at a higher temperature than the raw sea water and consequently, when the two combine the final temperature is somewhat higher then the assumed 60°F raw sea water input. Therefore, the heat that would have completely been used in heating raw input sea water, instead, heats only 20% of that amount due to the recirculation and thus, has heat left over that can be used in heating additional raw sea water. This increases the amount of sea water heated per unit of heat and thus increases the performance ratio (pounds of distillate produced per 1000 BTU of heat input) and the fresh water output. While this could have an effect of several hundred gallons of fresh water produced (for the size plant considered here), the per cent of the total is small. From a practical standpoint enough water is produced to justify the effort.

5.5 Results of the Analysis

The results of the analysis of the amount of fresh water produced are presented in Figures 5.7 and 5.8. Much more water is produced when using monoethanolamine, sodium hydroxide or lithium hydroxide as the carrier fluid than when using potassium carbonate. This can be explained by an analysis of the equations.

From Equation 5.28, the amount of fresh water produced is directly proportional to the heat released to the sea water in the boiler, Q_r. This heat is supplied by the heat released from the absorber and the carbonate cooler. While the carbonate cooler plays a part in the amount of heat available for desalting, as is similar to the case for the efficiency, the heat of reaction, generally, plays a more important role in the amount of heat released. The amount of fresh water produced is thus largely a function of the heat of reaction of the carrier fluid. This is verified by comparing the heats of reaction of each fluid with Figures 5.7 and 5.8. The highest heat of reaction is the one for sodium hydroxide and it likewise produces the most fresh water. The lowest heat of reaction in the 77 BTU per pound potassium carbonate, which also produces the least amount of fresh water.

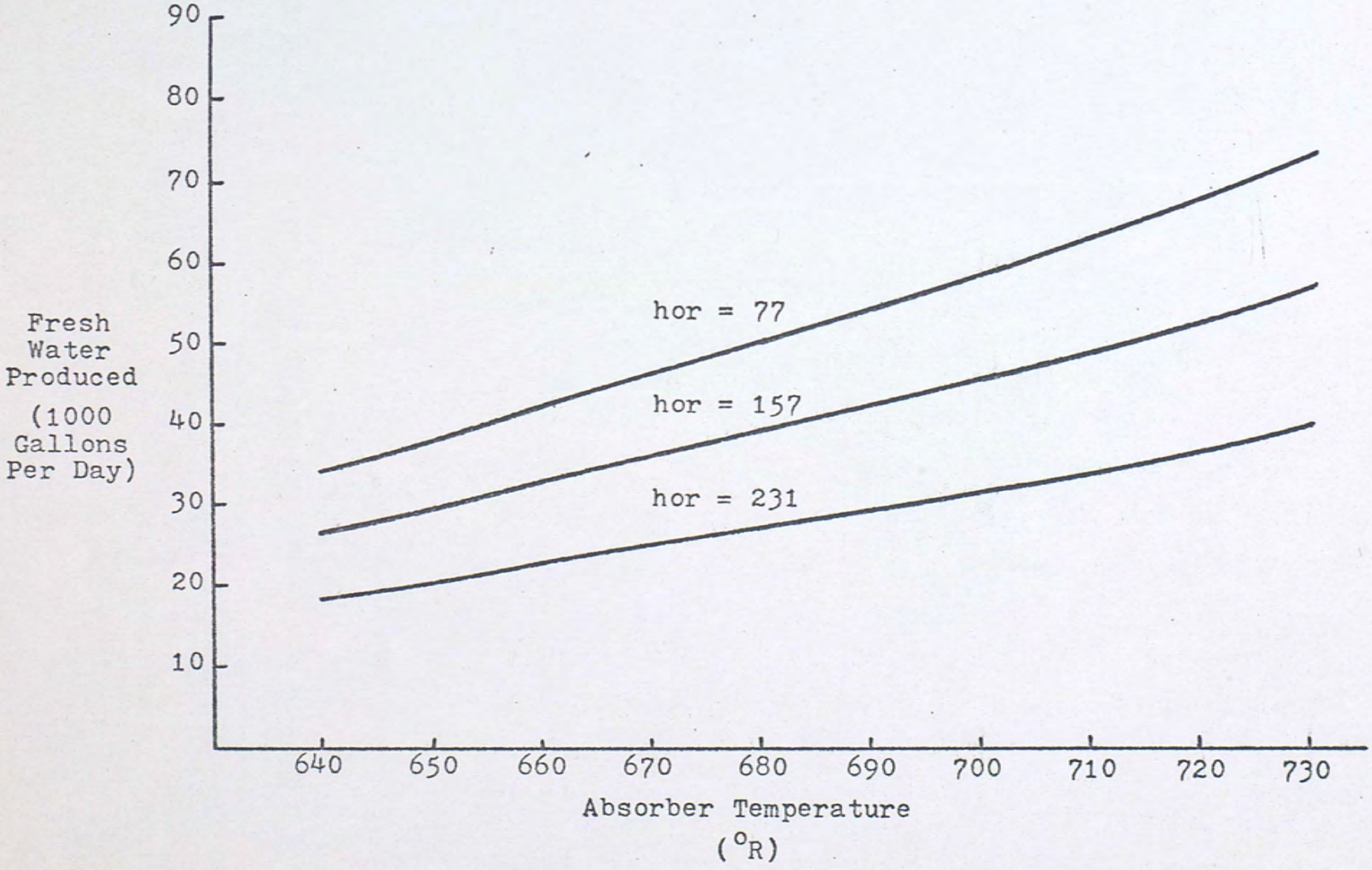

FIGURE 5.7 - Fresh Water Production for K_2CO_3

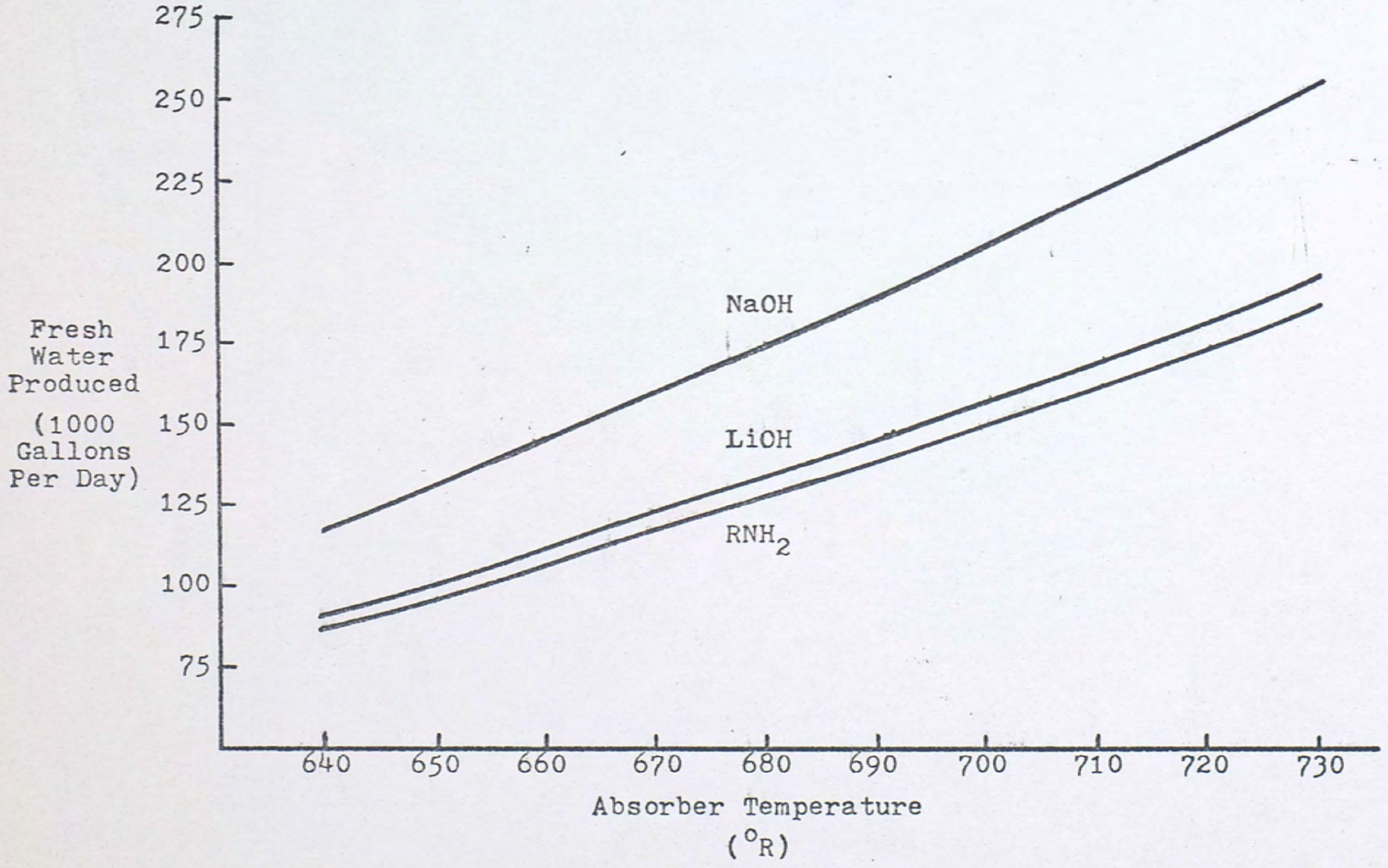

FIGURE 5.8 - Fresh Water Production for RNH_2, LiOH and NaOH

The results presented verify the fact stated earlier that the amount of sea water leaving the last stage of the desalination plant is approximately equal to nine-tenths of the amount entering the first stage. As stated earlier:

$$\omega_n \approx .9\omega_1 \qquad (5.35)$$

It is obvious that the mass of water lost by the sea water is the converted product or fresh water. Therefore, the amount of fresh water produced should be approximately one-tenth of the sea water circulated. A comparison of the values of the fresh water produced and the sea water circulated presented in Tables 5.1-5.4 verify Equation 5.35 fairly well. The fact that the results verify the equation, also implies that the results obtained agree fairly well with practical values. Although the absolute quantities could be much different from practical values, the fact that the ratios are approximately the same indicates that the values are at least a good approximation and that the equations derived are valid.

5.6 Rankine Cycle Comparison

In order to compare the binary aspects of the CO_2 cycle and conventional power cycles, an analysis was carried out to determine the efficiency and amount of fresh water

TABLE 5.1

RESULTS OF FRESH WATER CALCULATIONS, POTASSIUM CARBONATE

T_{out} (^{o}R)	640	650	660	670	680
hor (BTU/lb_m)	77	77	77	77	77
ΔT_{tot}	100	110	120	130	140
ω (gal/day)	525832.7	532324.6	538978.9	545801.3	552798.8
M_{tot} (gal/day)	18745.0	20874.0	23056.3	25293.9	27588.8
PR	1.8	2.0	2.1	2.3	2.5
hor (BTU/lb_m)	157	157	157	157	157
ΔT_{tot}	100	110	120	130	140
ω (gal/day)	756968.1	766313.0	775892.8	785714.0	795787.6
M_{tot} (gal/day)	26984.5	30049.4	33191.0	36412.0	39715.7
PR	1.8	2.0	2.1	2.3	2.5
hor (BTU/lb_m)	231	231	231	231	231
ΔT_{tot}	100	110	120	130	140
ω (gal/day)	970768.2	982753.4	995038.0	1007633.3	1020551.9
M_{tot} (gal/day)	34606.0	38536.7	42565.5	46696.4	50933.1
PR	1.8	2.0	2.1	2.3	2.5

TABLE 5.1 (Continued)

RESULTS OF FRESH WATER CALCULATIONS, POTASSIUM CARBONATE

T_{out} (^{o}R)	690	700	710	720	730
hor (BTU/lb_m)	77	77	77	77	77
ΔT_{tot}	150	160	170	180	190
ω (gal/day)	559977.9	567346.1	574910.4	582679.6	590661.6
M_{tot} (gal/day)	29943.3	32359.8	34840.6	37388.6	40006.4
PR	2.7	2.9	3.0	3.2	3.4
hor (BTU/lb_m)	157	157	157	157	157
ΔT_{tot}	150	160	170	180	190
ω (gal/day)	806122.3	816729.0	827618.4	838802.8	850293.3
M_{tot} (gal/day)	43105.1	46583.8	50155.2	53823.2	57591.6
PR	2.7	2.9	3.0	3.2	3.4
hor (BTU/lb_m)	231	231	231	231	231
ΔT_{tot}	150	160	170	180	190
ω (gal/day)	1033805.8	1047408.2	1061373.0	1075716.0	1090452.0
M_{tot} (gal/day)	55279.9	59741.1	64321.2	69025.1	73857.9
PR	2.7	2.9	3.0	3.2	3.4

TABLE 5.2

RESULTS OF FRESH WATER CALCULATIONS, MONOETHANOLAMINE

T_{out} (^{o}R)	640	650	660	670	680
hor (BTU/lb_m)	828.29	828.29	828.29	828.29	828.29
ΔT_{tot}	100	110	120	130	140
ω (gal/day)	2450316.0	2480570.0	2511577.0	2543370.0	2575978.0
M_{tot} (gal/day)	87349.3	97270.5	107439.7	117866.4	128550.4
PR	1.8	1.9	2.1	2.3	2.5

T_{out} (^{o}R)	690	700	710	720	730
hor (BTU/lb_m)	828.29	828.29	828.29	828.29	828.29
ΔT_{tot}	150	160	170	180	190
ω (gal/day)	2609429.0	2643764.0	2679014.0	2715218.0	2752413.0
M_{tot} (gal/day)	139532.0	150792.6	162353.3	174226.6	186425.1
PR	2.7	2.9	3.0	3.2	3.4

TABLE 5.3

RESULTS OF FRESH WATER CALCULATIONS, LITHIUM HYDROXIDE

T_{out} (^{o}R)	640	650	660	670	680
hor (BTU/lb_m)	876.22	876.22	876.22	876.22	876.22
ΔT_{tot}	100	110	120	130	140
ω (gal/day)	2566236.0	2597916.0	2630394.0	2663688.0	2697840.0
M_{tot} (gal/day)	91481.0	101872.0	112522.4	123442.3	134642.2
PR	1.8	1.9	2.1	2.3	2.5

T_{out} (^{o}R)	690	700	710	720	730
hor (BTU/lb_m)	876.22	876.22	876.22	876.22	876.22
ΔT_{tot}	150	160	170	180	190
ω (gal/day)	2732876.0	2768834.0	2805752.0	2843667.0	2882621.0
M_{tot} (gal/day)	146132.9	157926.1	170033.8	182468.7	195244.3
PR	2.7	2.9	3.0	3.2	3.4

TABLE 5.4

RESULTS OF FRESH WATER CALCULATIONS, SODIUM HYDROXIDE

T_{out} (^{o}R)	640	650	660	670	680
hor (BTU/lb_m)	1146.85	1146.85	1146.85	1146.85	1146.85
ΔT_{tot}	100	110	120	130	140
ω (gal/day)	3337891.0	3379102.0	3421340.0	3464650.0	3509067.0
M_{tot} (gal/day)	118989.7	132504.8	146357.4	160561.0	175128.6
PR	1.8	1.9	2.1	2.3	2.5

T_{out} (^{o}R)	690	700	710	720	730
hor (BTU/lb_m)	1146.85	1146.85	1146.85	1146.85	1146.85
ΔT_{tot}	150	160	170	180	190
ω (gal/day)	3554640.0	3601411.0	3649431.0	3698749.0	3479416.0
M_{tot} (gal/day)	190074.0	205414.0	221162.3	237336.4	253953.6
PR	2.7	2.9	3.0	3.2	3.4

produced from a comparable binary Rankine cycle power generation and sea water desalting plant. As in the CO_2 cycle, the desalting plant is a multistage flash distillation type.

A conventional method of obtaining heat from an electrical power generating plant to desalt sea water is illustrated in Figure 5.9. The process is exactly the same as the Rankine cycle except, some of the steam is extracted from the turbine at a convenient point and is used to heat sea water for desalination. The desalting plant replaces the condenser on this line and uses the heat rejected by the steam as it expands. It does the same job as the condenser, giving off latent heat generated by the steam in changing from vapor to liquid. The steam comes into the desalting plant at a higher temperature than it does to the condenser, but leaves both devices at the same conditions. Therefore, the desalting plant gives off more heat at a higher temperature which is necessary to heat sea water. The steam not extracted at this point continues expanding through the turbine and is finally passed to a conventional condenser. The two streams are rejoined and piped to the boiler where the process begins again.

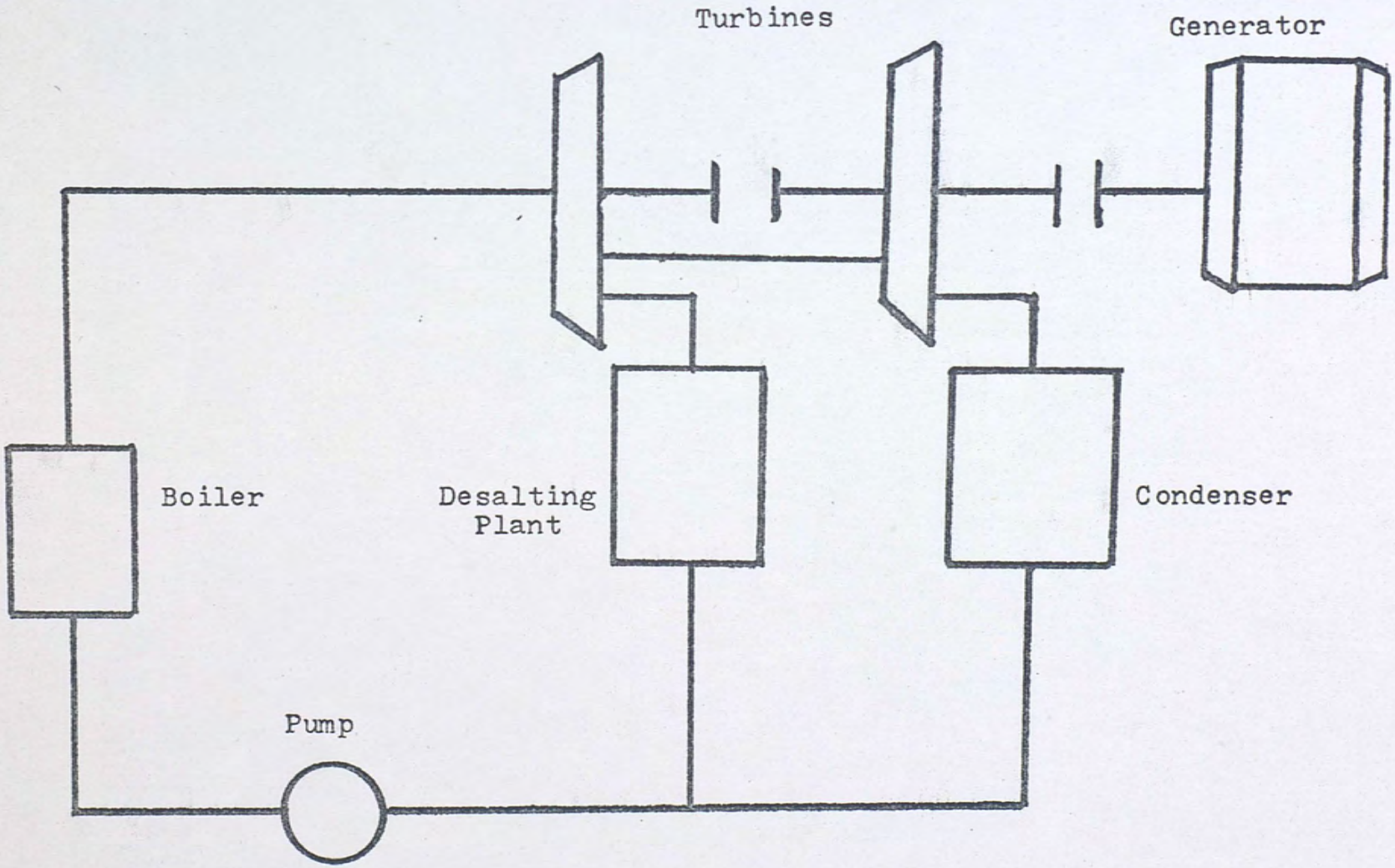

FIGURE 5.9 - Binary Rankine and Salt Water Distillation Cycle

It should be noted, that for this particular setup, the possibility of operating at either one of two extremes exists (Figure 5.10). The first extreme, which will be called case 1, is to allow all the steam to expand in the turbine and piping it to the condenser, producing no fresh water and maximum electricity. The second extreme, which will be called case 2, is to allow all the steam leaving the turbine to go through the desalting plant producing the maximum amount of fresh water and less electricity. This steam is at a higher temperature than that in an ordinary Rankine cycle condenser, to provide heat for desalination.

The third case, in which only part of the steam is diverted to the desalting plant, will not be examined due to the many different combinations of mass flows and turbine midstream and outlet temperatures possible. It can be shown, also, that it is not necessary to examine this case.

The Rankine cycle efficiency is given by (See Appendix A.6):

$$\eta_r = \frac{w_t \dot{m}_{H2O} - W_p}{Q_{cond} + w_t \dot{m}_{H_2O} - W_p} \qquad (5.36)$$

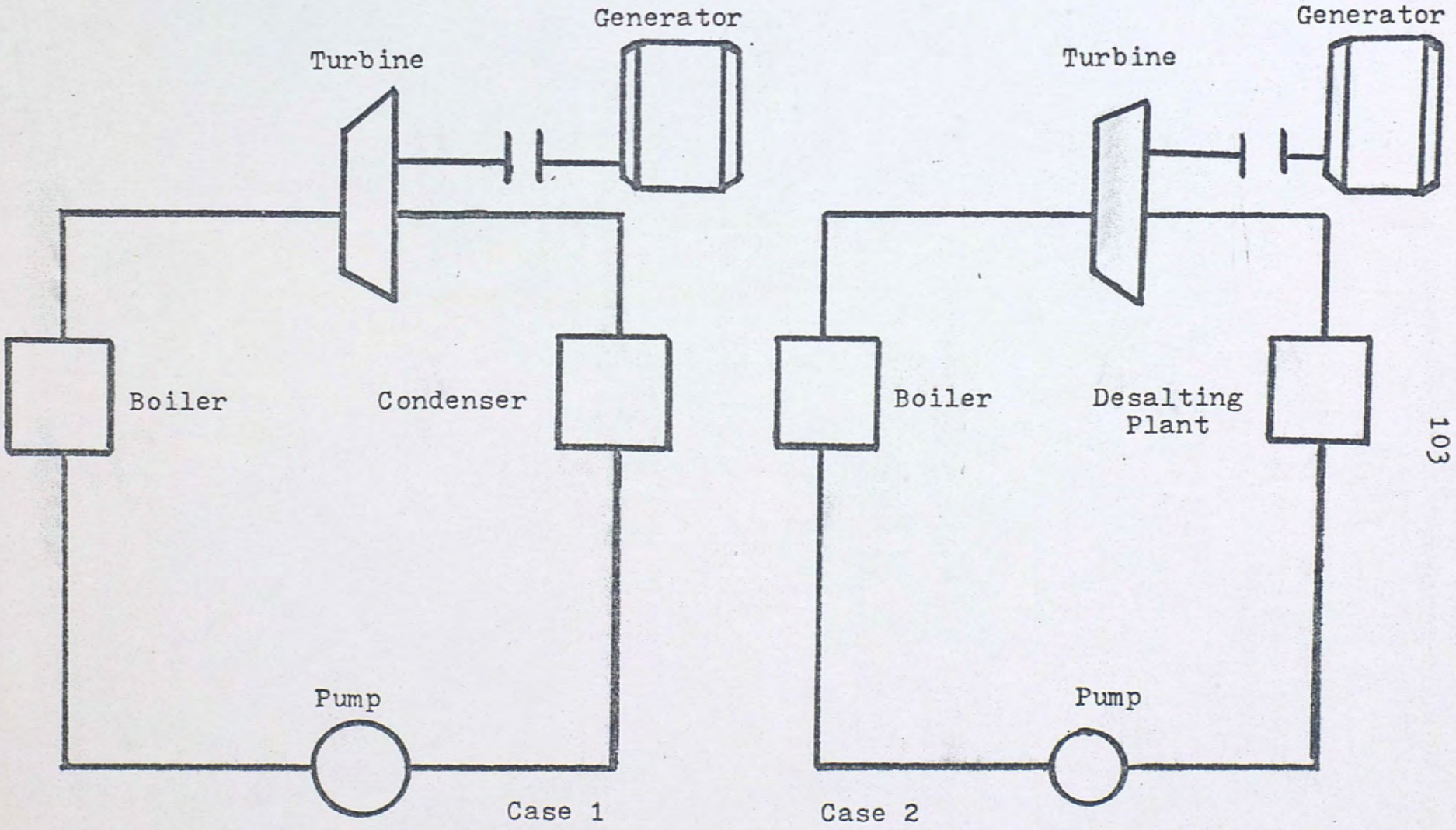

FIGURE 5.10 - Rankine Cycle, Case 1 and Case 2

Where Q_{cond} = Heat given off by the condenser

$\dot{m}_{H_2O}$ = Mass flow rate of the steam

w_t = Work of the turbine per unit mass

W_p = Work of the pump per unit time

η_r = Rankine cycle efficiency

The fresh water production is given by Equation 5.28 which says the amount of water produced is directly proportional to the heat applied.

From Equation 5.36, it is obvious that the maximum efficiency occurs for maximum turbine work and minimum condenser heat loss. This corresponds to case 1 where the steam gives up most of its energy in the turbine and little in the condenser. This is also the case of minimum fresh water production, due to the fact that the turbine exit temperature is too low to heat sea water to a sufficiently high temperature. The minimum efficiency occurs for minimum turbine work and maximum condenser heat loss. This is the condition of case 2 where the steam exits from the turbine at a high temperature and enters directly into the desalting plant. The high temperature minimizes the turbine work and maximizes the heat released in the desalting plant (which acts as the condenser in

this case). This, thereby, maximizes the amount of fresh water produced.

From the above, any condition between case 1 and case 2 (i.e. case 3), would be a compromise between maximum efficiency and maximum fresh water output. This will be made clearer with a numerical example below.

It should also be noted that when steam is mentioned in reference to the desalting plant, it is used solely in the desalting plant boiler to heat the sea water. Once losing its heat, it is recirculated through the Rankine cycle and does not become a part of the distillation cycle.

The comparison is based on maintaining an equal power output in the CO_2 and Rankine cycles, with the same turbine inlet temperatures. The operating conditions for the Rankine cycle are shown in Table 5.5. The turbine inlet temperature and the power output are the same as for the CO_2 cycle and both conditions are kept constant. The condenser exit conditions (or the desalting plant exit conditions, depending on which case is being considered) are kept constant at $100^{\circ}F$ saturated liquid (typical for

TABLE 5.5

RANKINE CYCLE CONDITIONS

Without Desalting

Turbine Inlet	1000°F	1870 psia
Turbine Exit	100°F	saturated vapor
Condenser Exit	100°F	saturated liquid
Pump Exit	100°F	1870 psia
Boiler Exit	1000°F	1870 psia

With Desalting

Turbine Inlet	1000°F	1870 psia
Turbine Exit	110-270°F	saturated vapor
Desalting Plant Exit	100°F	saturated liquid
Pump Exit	100°F	1870 psia
Boiler Exit	1000°F	1870 psia

conventional cycles). If the above conditions are specified, the turbine outlet will control the values of the other parameters in the system, including the efficiency. The turbine outlet temperature is varied over a range of temperatures, while the above parameters remain constant, to determine the effect on the efficiency and fresh water production. The results are presented in Table 5.6 and Figures 5.11 and 5.12.

The first column in Table 5.6 is case 1 in which no fresh water is produced. This is the case of maximum power generation efficiency. All the steam is used in the turbine to generate power. The maximum efficiency that could be expected out of this cycle, therefore, is 25.4%. This is lower than the average rankine cycle plant, but this cycle does not include regeneration, reheat, an economizer or any other efficiency improving methods used in conventional plants. The CO_2 cycle examined in this report, however, also does not include them.

The rest of the data show results for case 2. The distillation plant replaces the condenser and all the steam from the turbine is used to heat sea water for desalination. The turbine outlet temperature is varied to provide more

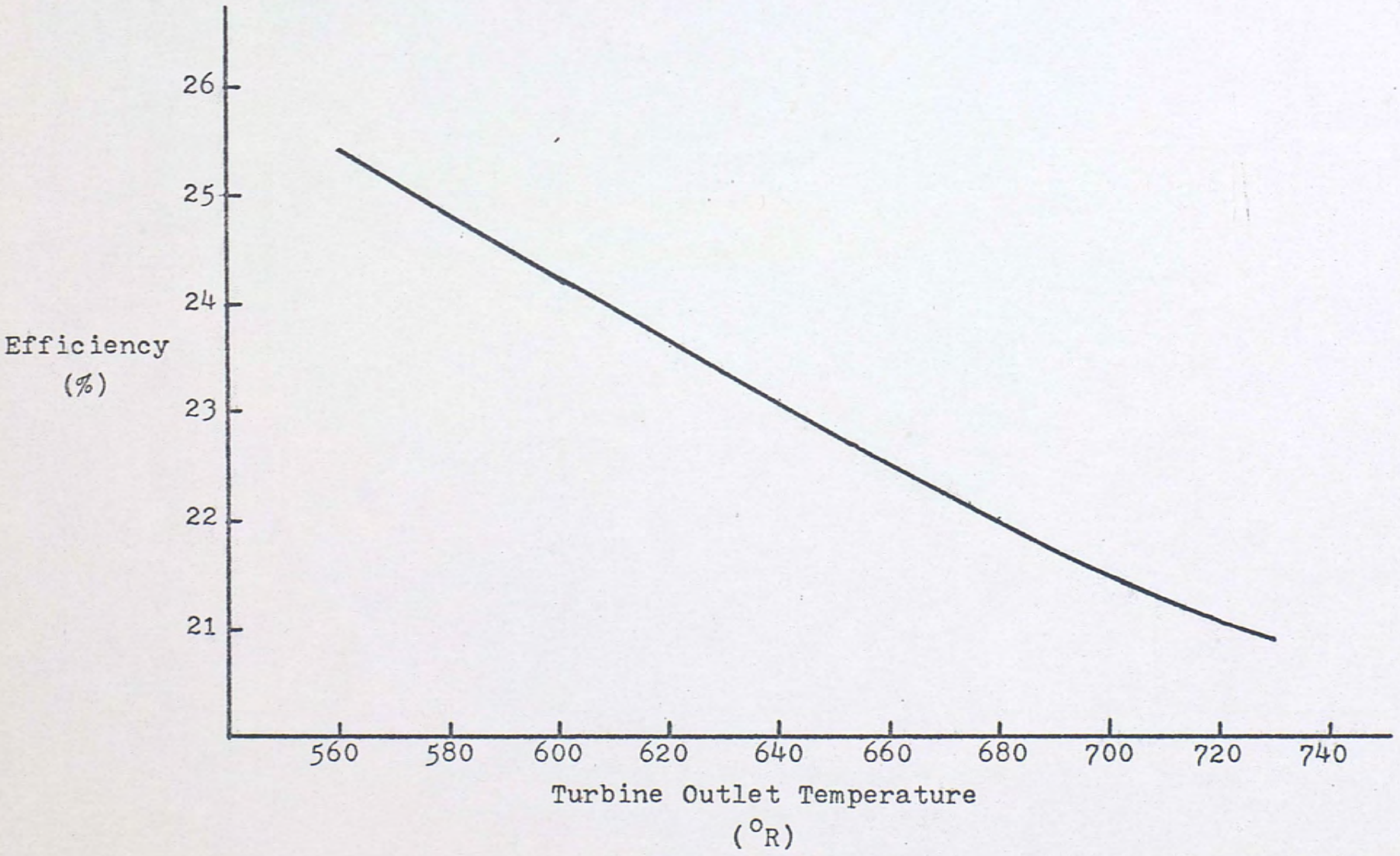

FIGURE 5.11 - Rankine Cycle Efficiency

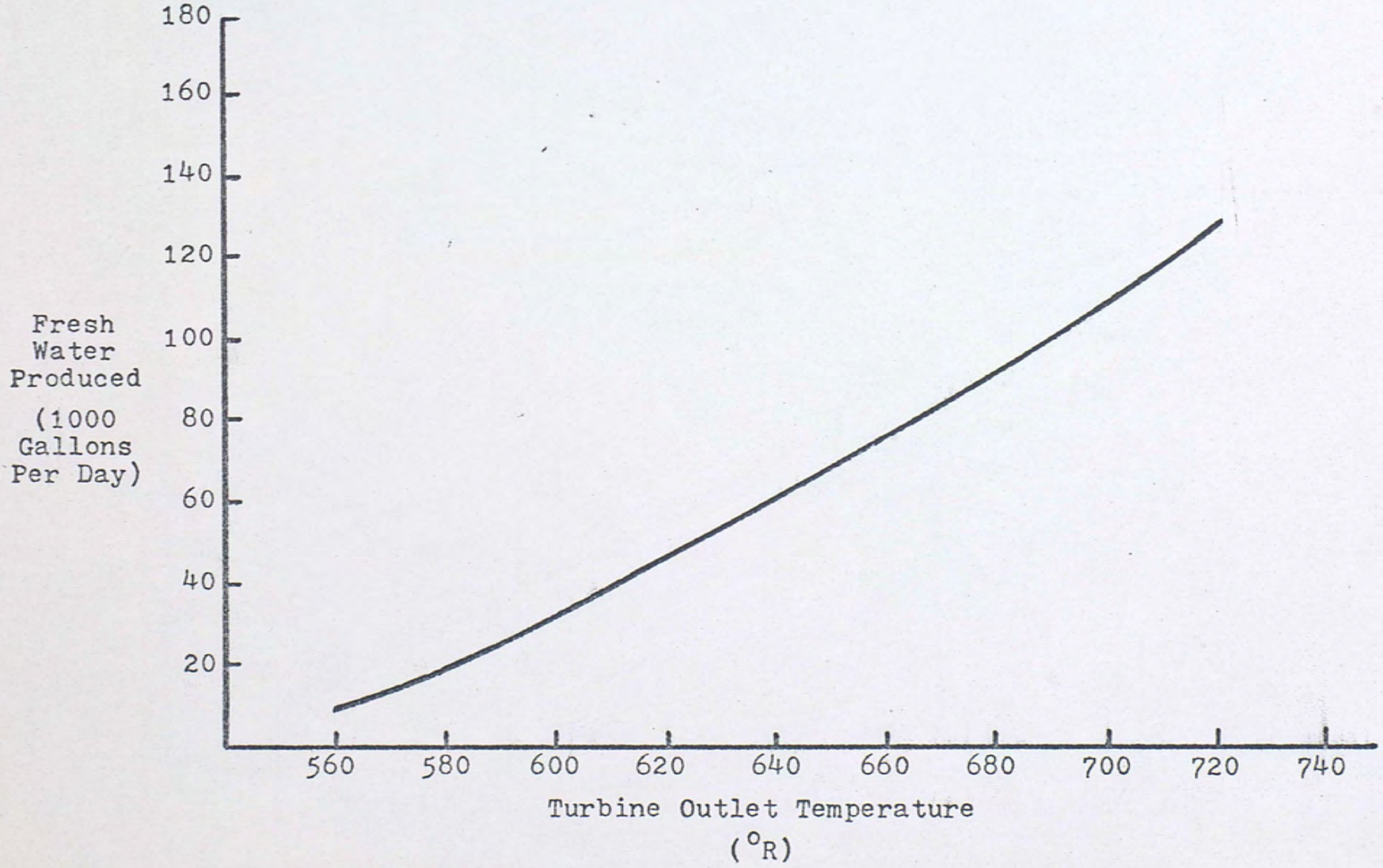

FIGURE 5.12 - Rankine Cycle Fresh Water Production

TABLE 5.6

RESULTS OF RANKINE CYCLE CALCULATIONS

T_{out} (^{o}R)	560	570	580	590	600	610
T_{in} (^{o}R)	1460	1460	1460	1460	1460	1460
P_{out} (psia)	.949	1.275	1.693	2.223	2.889	3.718
P_{in} (psia)	1870	1870	1870	1870	1870	1870
$\dot{m}_{H_2O}$ (lb_m/hr)	9531.8	9641.8	9751.8	9864.3	9976.6	10091.5
η_r	.254	.251	.248	.245	.242	.240
ω (gal/day)	1386660.0	1422007.0	1457645.0	1494105.0	1530853.0	1568445.0
M (gal/day)	9886.4	15207.6	20784.9	26631.1	32743.3	39138.5
PR	.357	.535	.713	.891	1.069	1.248

TABLE 5.6 (Continued)

RESULTS OF RANKINE CYCLE CALCULATIONS

T_{out} (^{o}R)	620	630	640	650	660	670
T_{in} (^{o}R)	1460	1460	1460	1460	1460	1460
P_{out} (psia)	4.741	5.993	7.511	9.340	11.526	14.123
P_{in} (psia)	1870	1870	1870	1870	1870	1870
$\dot{m}_{H_2O}$ (lb_m/hr)	10209.2	10326.6	10443.7	10563.5	10686.0	10808.3
η_r	.236	.234	.231	.228	.226	.223
ω (gal/day)	1606915.0	1645674.0	1684697.0	1724617.0	1765462.0	1806572.0
M (gal/day)	45826.8	52798.7	60056.4	67627.4	75522.6	83721.3
PR	1.426	1.604	1.782	1.961	2.139	2.317

TABLE 5.6 (Continued)

RESULTS OF RANKINE CYCLE CALCULATIONS

T_{out} (^{o}R)	680	690	700	710	720	730
T_{in} (^{o}R)	1460	1460	1460	1460	1460	1460
P_{out} (psia)	17.186	20.780	24.968	29.825	35.427	41.858
P_{in} (psia)	1870	1870	1870	1870	1870	1870
$\dot{m}_{H_2O}$ (lb_m/hr)	10929.9	11051.0	11171.3	11294.3	11412.7	11533.7
η_r	.220	.218	.215	.213	.211	.208
ω (gal/day)	1847915.0	1889466.0	1931188.0	1973829.0	2015815.0	2058693.0
M (gal/day)	92224.7	101033.9	110149.3	119617.7	129348.2	139438.3
PR	2.495	2.674	2.852	3.030	3.208	3.386

or less heat for desalination and the effect on the efficiency and fresh water production are calculated. As mentioned earlier, turbine outlet temperatures below 180°F (82.2°C) are not feasible for desalination. The data is presented, however, as the result of the calculations.

If a comparison is made between the binary Rankine cycle and the binary CO_2 cycle, using potassium carbonate as the carrier fluid, the advantages of the latter are obvious. For example, from Figures 4.1 and 5.7, for the CO_2 cycle to produce 40,000 gallons of fresh water per day, depending on whether the heat of reaction of 77, 157 or 231 BTU per pound is valid, the absorber temperatures (turbine outlet temperature) must be respectively 730, 680 or 654 degrees Rankine, producing the respective cycle efficiencies of 42.75%, 34.8% and 29.7%. From Figures 5.11 and 5.12, for the Rankine cycle to produce 40,000 gallons of fresh water per day, the turbine outlet temperature must be 610 degrees Rankine, producing a cycle efficiency of 23.9%. Although the turbine outlet temperatures must be higher, the CO_2 cycle has a higher efficiency than the Rankine cycle when producing the same amount of fresh water.

It can be seen now why case 3 need not be considered. The binary Rankine cycle operates at 23.9% efficiency to produce 40,000 gallons of water per day. If case 3 were considered, some of the steam would be allowed to expand completely through the turbine, increasing the efficiency, and allowing less of the steam to go to the desalting plant, lowering the amount of fresh water produced. This is the same result that would occur if the turbine outlet temperature were lowered. No matter how the parameters are varied, however, the maximum efficiency that could possibly be generated by the Rankine cycle is 25.4%. The CO_2 cycle operates at better efficiencies and at the same time, produces a substantial amount of fresh water.

The Rankine cycle does fair better when compared with the other carrier fluids. A comparison is made against the highest efficiency producing carrier fluid of the other three, monoethanolamine. To produce 140,000 gallons of fresh water per day, monoethanolamine must have a turbine outlet temperature of 690 degrees Rankine, producing an efficiency of 15%. To produce the same amount of water, the Rankine cycle must have a turbine outlet temperature of 730 degrees Rankine, which produces an efficiency of 20.8%. The Rankine cycle efficiency is almost 6% better

than that of monoethanolamine for the same fresh water output. Comparing Figures 4.2 and 5.8, similar results could be obtained for the other carrier fluids.

CHAPTER 6

CONCLUSIONS

The CO_2 cycle offers two main advantages over the conventional power generating cycles. It can produce power at efficiencies well above those of conventional power plants and at the same time produce fresh water. The results of this study verify the fact that the cycle warrants further study. The Rankine cycle has undergone extensive study over the past few years and it is doubtful that any significant increase in efficiency can be obtained. If the same amount of study were accorded the CO_2 cycle, which in certain cases has an efficiency of 44%, and with the inclusion of efficiency improving methods such as reheat and regeneration which improve the efficiency by several per cent[15], it is conceivable that the CO_2 cycle could approach efficiencies of 50%. This number would be extremely difficult to reach in the case of the Rankine cycle.

The increased power generation efficiency is desirable in any part of the world, but the plant would be especially

useful in arid areas where fresh water is scarce but salt water is abundant. The plant would generate electrical power for the community and at the same time produce fresh water to supplement the available scarce supply.

Specific recommendations for further study are:

1. Experimental investigation into the temperature-pressure characteristics of the regeneration process.
2. Experimental investigation into the absorption characteristics of the carrier fluids at low pressure.
3. Pilot plant studies to verify cycle efficiencies.
4. Investigate waste heat utilization for other than desalination such as low temperature refrigeration.
5. Economic analysis of the CO_2 cycle for comparison against conventional Rankine power cycles.
6. Investigation into the chemical kinetics which take place in the absorber and regenerator.
7. Investigate the efficiency enhancement techniques such as regeneration, reheat, and economizer processes.

APPENDIX A

A.1 Justification of $\Delta h = c_p \Delta T$ for water and the carrier fluids.

The justification is best presented by examining the steam tables. The enthalpies for saturated liquid water, at various temperatures, are given in Table A.1. Since the c_p for water is approximately one, the approximation for Δh reduces to (keeping in mind the units):

$$\Delta h = \Delta T \qquad (A.1)$$

Table A.1 verifies Equation A.1 very well. A ten degree temperature change corresponds very closely to a ten BTU per pound enthalpy change.

This same assumption can be made for any of the carrier fluids. This assumption is usually good for most liquids (at certain conditions) and it is assumed to apply for these fluids.

A.2 Derivation of $\Delta h = c_p \Delta T$ for a perfect gas.

The equation of state of a perfect gas is given by:

TABLE A.1

STEAM TABLE EXERPT

Temperature (^{o}F)	Saturation Pressure (psia)	Enthalpy (BTU/lb_m)
60	.2563	28.06
70	.3631	38.04
80	.5069	48.02
90	.6982	57.99
100	.9492	67.97
110	1.2748	77.94
120	1.6924	87.92
130	2.2225	97.90
140	2.8886	107.89
150	3.718	117.89
160	4.741	127.89
170	5.992	137.90
180	7.510	147.92
190	9.339	157.95
200	11.526	167.99
210	14.123	178.05
212	14.696	180.07

$$Pv = \mathbb{R}T \qquad (A.2)$$

Where P = Pressure

v = Specific volume

$\mathbb{R}$ = Gas constant

T = Temperature

It is also given, that for a perfect gas, the internal energy is a function of temperature only:

$$u = u(T) \qquad (A.3)$$

Where u = Internal energy

From the definition of enthalpy:

$$h = u + Pv \qquad (A.4)$$

Substituting for Pv from Equation A.2:

$$h = u + \mathbb{R}T \qquad (A.5)$$

Since u is a function of temperature only and $\mathbb{R}$ is a constant, h is a function of temperature only. The relation between the enthalpy and temperature can be found by use of the definition of specific heat at constant pressure:

$$c_p = \left(\frac{\partial h}{\partial T}\right)_P \qquad (A.6)$$

Since h is a function of temperature only and is not a function of pressure:

$$c_p = \frac{dh}{dT} \qquad (A.7)$$

Rearranging:

$$dh = c_p dT \qquad (A.8)$$

Integrating between two arbitrary points:

$$\Delta h = c_p \Delta T \qquad (A.9)$$

The enthalpy difference between two points is equal to the specific heat at constant pressure times the temperature change between these two points.

A.3 Theoretical calculation of ratio for potassium carbonate.

The derivation is based on the chemical reaction given by Equation 4.1:

$$\underset{138}{K_2CO_3} + \underset{18}{H_2O} + \underset{44}{CO_2} \rightleftharpoons \underset{200}{2KHCO_3} \qquad (4.1)$$

Directly underneath each compound is the molecular weight. If it is assumed that one pound mole of each compound

(two pound moles of $KHCO_3$) is present, the molecular weight then becomes the number of pounds.

For practical considerations, Equation 4.1 must be altered. In the CO_2 cycle, the $KHCO_3$ is circulated in a solution of water. The reaction thus becomes:

$$K_2CO_3 + x(H_2O) + CO_2 \rightleftharpoons 2KHCO_3 + (x - 1)H_2O \qquad (A.10)$$

The value of x is determined by solubility considerations. The solubility of $KHCO_3$ at approximately the temperatures encountered in the CO_2 cycle is about 41 pounds of $KHCO_3$ per 100 pounds of solution. Therefore:

$$\frac{41 \text{ pounds } KHCO_3}{100 \text{ pounds solution}} =$$

$$\frac{200 \text{ pounds } KHCO_3}{200 \text{ pounds } KHCO_3 + (x - 1) \text{ pounds } H_2O} \qquad (A.11)$$

$$x = 288.8 \text{ pounds } H_2O$$

Since there are 18 pounds of H_2O per pound mole, x in terms of moles is:

$$x = \frac{288.8 \text{ pounds } H_2O}{18 \text{ pounds } H_2O/\text{mole}} \qquad (A.12)$$

$$x = 16 \text{ moles}$$

Equation A.10 becomes:

$$K_2CO_3 + 16H_2O + CO_2 \rightleftharpoons 2KHCO_3 + 15H_2O \qquad (A.13)$$

The ratio of pounds of carrier fluid ($K_2CO_3 + H_2O$) to pounds of CO_2 is:

$$R = \frac{138 \text{ pounds } K_2CO_3 + 16X18 \text{ pounds } H_2O}{44 \text{ pounds } CO_2} \qquad (A.14)$$

$$R = 10 \frac{\text{pounds carrier fluid}}{\text{pound } CO_2}$$

A.4 Theoretical calculation of heat of reaction for potassium carbonate.

The heat of reaction is determined from the chemical reaction by the heat of formation of the products minus the heat of formation of the reactants. In other words:

$$2KHCO_3 \rightleftharpoons K_2CO_3 + H_2O + CO_2 + \Delta H \qquad (A.15)$$

Where ΔH = Heat of reaction

Using heats of formation from the tables :

$$2(945) = 1181 + 286.2 + 414.9 + \Delta H \qquad (A.16)$$

The units are kilojoules per gram formula weight.

Solving for ΔH:

$$\Delta H = 7.9 \frac{\text{kilojoules}}{\text{gram formula weight}}$$

Changing units:

$$\Delta H = 7.9 \frac{kj}{gfw} \times .95 \frac{BTU}{kj} \times \frac{454}{44} \frac{gfw}{\text{pound } CO_2}$$

$$\Delta H = 77 \frac{BTU}{\text{pound } CO_2}$$

A.5 Derivation of Equation 5.18.

The energy change across a boiler can be derived by application of the First Law of Thermodynamics:

$$\Delta e = q - w \qquad (A.17)$$

Where Δe = Change in energy of the system

q = Heat transfer to the system

w = Work done by the system

There is no work done by the boiler so Equation A.17 becomes:

$$\Delta e = q \qquad (A.18)$$

The energy change is given by the change in internal

energy, kinetic energy, potential energy and flow energy. These quantities are given by:

$$\text{Internal Energy} = u \tag{A.19}$$

$$\text{Kinetic Energy} = \frac{\text{⊽}^2}{2g_c} \tag{A.20}$$

$$\text{Potential Energy} = z \tag{A.21}$$

$$\text{Flow Energy} = pv \tag{A.22}$$

Where g_c = Gravitational constant

⊽ = Velocity of the fluid

z = Height above the datum

v = Specific volume

p = Pressure

Substituting Equations A.19-A.22 into Equation A.18:

$$u_i + \frac{\text{⊽}_i^2}{2g_c} + z_i + p_i v_i + q = u_o + \frac{\text{⊽}_i^2}{2g_c} + z_o + p_o v_o \tag{A.23}$$

Where the subscript i denotes the boiler inlet and o the boiler exit.

The kinetic energy change due to change in velocity is zero and it is assumed that there is no change in eleva-

tion. The quantity u + pv is defined as the specific enthalpy. Equation A.23 thus reduces to:

$$q = h_o - h_i \qquad (A.24)$$

Equation A.24 describes the amount of heat added to the boiler in terms of the enthalpy difference of the exit and inlet streams. To obtain the amount of heat added per unit time, Equation A.24 is multiplied by the mass flow rate of the fluid:

$$Q = \dot{m}\Delta h \qquad (A.25)$$

Where Q = Heat added to the boiler per unit time

$\dot{m}$ = Mass flow rate of the fluid

Δh = $h_o - h_i$

Equation A.25 assumes that the boiler efficiency is 100%.

A.6 Derivation of Equation 5.36.

The efficiency for any cycle is given by Equation 3.28:

$$\eta = \frac{W_{net}}{Q_{added}} \qquad (3.28)$$

The net work for the Rankine cycle (Figure A.1) is the difference in the turbine work and the pump work:

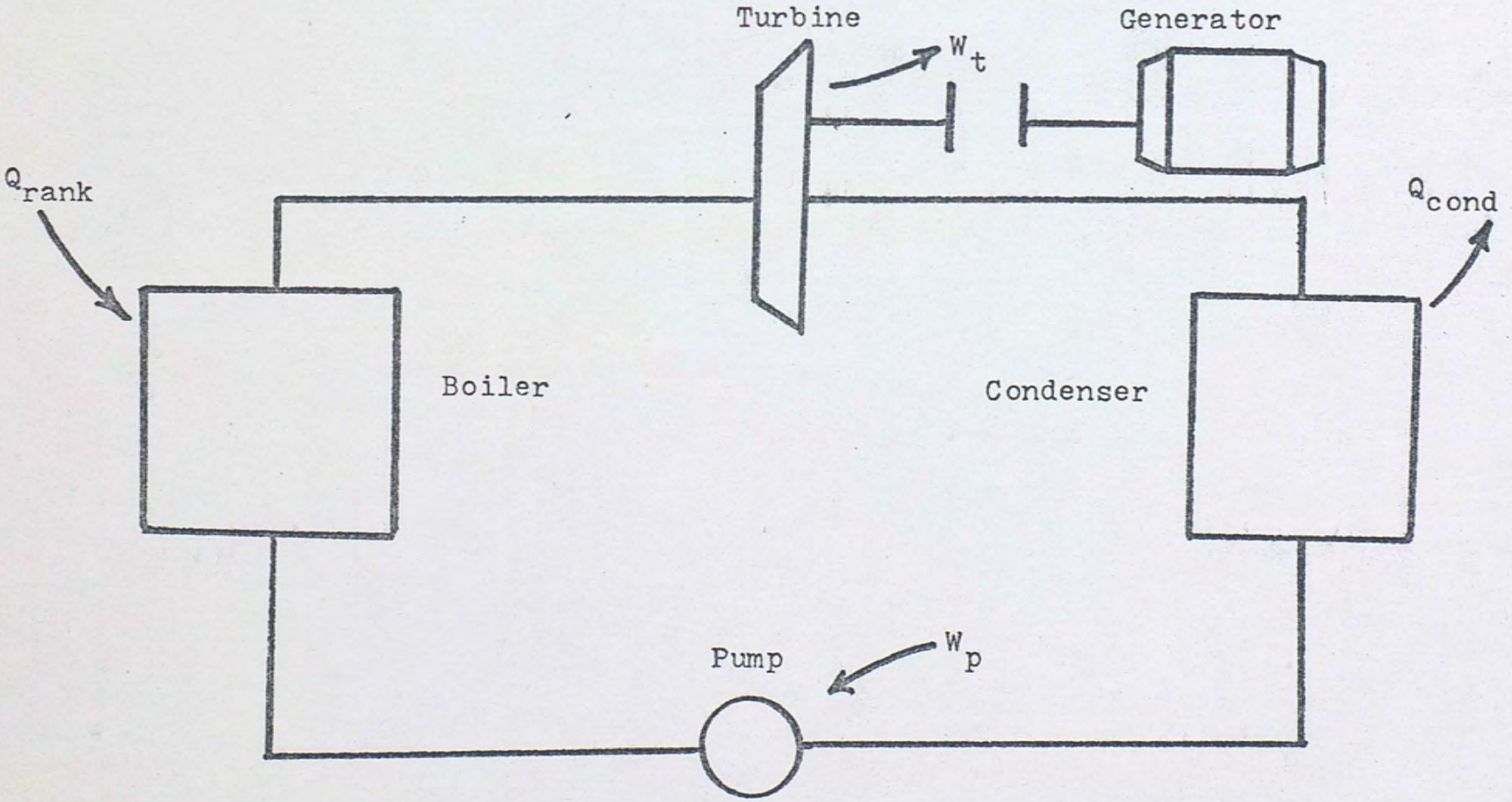

FIGURE A.1 - Rankine Cycle

$$W_{net} = w_t \dot{m}_{H_2O} - W_p \qquad (A.26)$$

Where W_{net} = Net work per unit time

w_t = Turbine work per unit mass

$\dot{m}_{H_2O}$ = Steam mass flow rate

W_p = Work of the pump per unit time

The heat added to the system is the heat added to the boiler, Q_{rank}. An equation for Q_{rank} can be determined by writing a heat balance for the cycle:

$$Q_{rank} + W_p = w_t \dot{m}_{H_2O} + Q_{cond} \qquad (A.27)$$

Where Q_{cond} = Heat lost by the condenser per unit time

Solving for Q_{rank}:

$$Q_{rank} = w_t \dot{m}_{H_2O} + Q_{cond} - W_p \qquad (A.28)$$

Substituting Equations A.26 and A.28 into Equation 3.28, the Rankine cycle efficiency becomes:

$$\eta_r = \frac{w_t \dot{m}_{H_2O} - W_p}{w_t \dot{m}_{H_2O} + Q_{cond} - W_p} \qquad (A.29)$$

APPENDIX B

The computer program was written to aid in the calculations and to make it possible to look at a wide range of different values of data. The CO_2 cycle computer program follows:

```
      DIMENSION A(10,100),B(10,100)
      REAL KQLS,KQL,KWREQ,LAMDAM,M,KQIN
C     N IS THE NUMBER OF CASES TO BE ANALYZED
      READ(5,999) N
  999 FORMAT(I3)
      LL=1
      KK=1
      DO 1 I=1,N
      KK=KK+2
      K=0
      LL=LL+1
      DO 5 JJ=1,10
      IF (K .GE. 5) GO TO 310
C     CYCLE IS THE GAS THROUGH THE TURBINE, FLUID
C     IS THE CARRIER LIQUID
      READ(5,51) CYCLE,F,L,UID
   51 FORMAT(A3,3A4)
  310 WRITE(6,52) CYCLE
   52 FORMAT('1','THE FOLLOWING IS FOR A ',A3,'
     1CYCLE')
```

```
C     ALL TEMPERATURES AND PRESSURES ARE IN ABSOLUTE
C     UNITS, TIN IS THE TURBINE INLET TEMPERATURE,
C     TOUT IS THE TURBINE OUTLET TEMPERATURE, PIN
C     IS ALLOWED TO FLOAT, POUT IS THE TURBINE
C     OUTLET PRESSURE, CP IS THE SPECIFIC HEAT OF
C     THE GAS THROUGH THE TURBINE, R IS THE GAS
C     CONSTANT, EFF IS THE TURBINE ISENTROPIC
C     EFFICIENCY, AND P IS THE DESIRED OUTPUT FROM
C     THE TURBINE
      IF (K .GE. 5) GO TO 325
    7 READ(5,100) TIN,TOUT,POUT,CP,R,EFF,P
  100 FORMAT(7F10.3)
  325 TOUT=TOUT + 10.
    8 TISEN=TIN-((TIN-TOUT)/CP)
    9 WTURB=CP*(TIN-TOUT)
      WTS=WTURB/EFF
      TOUTS=-(WTS/CP) + TIN
   10 PIN=POUT/(TOUTS/TIN)**(CP/R)
   11 WRITE(6,101) TIN,PIN
  101 FORMAT(31HOTHE INLET CONDITIONS ARE,T(R)=,
     1F10.3,9H P(PSIA)=,F10.3)
      WRITE(6,997)TOUT,POUT
  997 FORMAT(32HOTHE OUTLET CONDITIONS ARE,T(R)=,
     1F10.3,9H P(PSIA)=,F10.3)
   12 XCOTO=P*3412/WTURB
      AP=P*3412
      WRITE(6,102) AP,P
  102 FORMAT('0','THE TURBINE OUTPUT IS'F15.3,
     1'BTU/HR =',F10.3,' KW')
      WRITE(6,103)XCOTO
  103 FORMAT('0','THE REQUIRED MASS FLOW RATE IS',
     1F10.3,' LBM/HR')
```

```
C       TABS IS THE ABSORBER TEMPERATURE IN DEGREES
C       RANKINE, HT IS THE HEAT OF REACTION IN THE
C       ABSORBER, PER POUND OF GAS ABSORBED
        IF (K .GE. 5) GO TO 311
   16   READ(5,401)TABS,HT
  401   FORMAT(2F10.3)
  311   TABS=TABS + 10.
   17   QLOSS=(HT-(TABS-TOUT)*CP)*XCOTO
C       CONC IS THE PERCENTAGE CONCENTRATION OF
C       CARRIER FLUID IN WATER, WHILE RATIO IS THE
C       RATIO OF LBM OF CARRIER FLUID TO LBM OF GAS
        IF (K .GE. 5) GO TO 19
   18   READ(5,402) CONC,RATIO
  402   FORMAT(2F10.3)
   19   XCARB=RATIO*XCOTO
   20   XIX=XCOTO + XCARB
        WRITE(6,603) F,L,UID,CYCLE,RATIO
  603   FORMAT('0','THE RATIO OF LBM',3A4,'TO LBM ',
       1A3,' IS',F10.3)
        WRITE(6,998) HT,CYCLE
  998   FORMAT('0','THE HEAT OF REACTION IS',F10.3,
       1'PER LBM ',A3,' ABSORBED')
        WRITE(6,996) TABS
  996   FORMAT(26HOTHE ABSORBER TEMPERATURE IS,F10.3,
       1'(R)')
        KQLS=QLOSS/3412
        Z=QLOSS/XCOTO
   31   WRITE(6,403) QLOSS,KQLS,Z
  403   FORMAT('0','HEAT LOSS IN ABSORBER IS',F15.3,
       1' BTU/HR =',F10.3,' KW',5X,'PER LBM=',F10.3,
       2' BTU')
```

```
C     VMIX IS THE SPECIFIC VOLUME OF THE COMBINED
C     GAS AND CARRIER FLUID, EFFP IS THE PUMP
C     EFFICIENCY, VCARB IS THE SPECIFIC VOLUME OF
C     THE CARRIER FLUID, EFFW IS THE PELTON WHEEL
C     EFFICIENCY
      IF (K .GE. 5) GO TO 24
   23 READ(5,201) VMIX,EFFP,VCARB,EFFW
  201 FORMAT(4F10.4)
   24 WPUMP=VMIX*(PIN-POUT)*XIX*144/(EFFP*778.16)
   25 WPELT=VCARB*(PIN-POUT)*XCARB*EFFW*144/778.16
      WRITE(6,798) WPUMP
  798 FORMAT(F20.10)
   26 WREQ=WPUMP-WPELT
   27 WNET=((WTURB*XCOTO)-WREQ)/3413
      KWREQ=WREQ/3412
      WRITE(6,202) WREQ,KWREQ
  202 FORMAT('0','POWER REQUIRED BY THE PUMP-PELTON
     1WHEEL COMBINATION IS',F15.2,'BTU/HR=',F10.3,
     `2' KW')
      BWR=WREQ/(WTURB*XCOTO)
      WRITE(6,801) BWR
  801 FORMAT('0','THE BACKWORK RATIO IS',F5.4)
      ANET=WNET*3412
      WRITE(6,203) ANET,WNET
  203 FORMAT('0','THE NET POWER OUTPUT IS',F15.3,
     1' BTU/HR=',F10.3," KW')
C     DELTC IS THE TEMPERATURE DIFFERENCE ACROSS THE
C     CARRIER FLUID COOLER, CPCARB IS THE SPECIFIC
C     HEAT OF THE CARRIER FLUID
      IF (K .GE. 5) GO TO 35
   34 READ(5,301) DELTC,CPCARB
  301 FORMAT(2F10.3)
```

```
 35 QCOOL=DELTC*CPCARB*XCARB
    KQL=QCOOL/3412
    Y=QCOOL/XCARB
 36 WRITE(6,302) F,L,UID,QCOOL,KQL,Y
302 FORMAT('0','HEAT LOSS IN THE ',3A4,' COOLER
   1IS',F15.3,' BTU/HR=',F10.3,' KW',5x,' PER
   2LBM=',F10.3,' BTU')
    QIN=QLOSS + (WNET*3412) + QCOOL
    KQIN=QIN/3412
    WRITE(6,41) QIN,KQIN
 41 FORMAT('0','TOTAL Q IN IS',F15.3,' BTU',
   1F15.3,' KW')
    HR=QIN/WNET
    WRITE(6.42) HR
 42 FORMAT('0','THE HEAT RATE IS',F15.3,'
   1BTU/KW')
 39 BETA=(WNET*3412)/(QLOSS + (WNET*3412) +
   1QCOOL)
    CETA=(TIN-TOUT)/TIN
703 WRITE(6,602) CETA
602 FORMAT(31H0THE CARNOT CYCLE EFFICIENCY IS,
   1F10.3)
 40 WRITE(6,501) CYCLE,BETA
501 FORMAT('0','THE ',A3,' CYCLE EFFICIENCY IS',
   1F10.3)
    LAMDAM=1000.
    CPW=1.
    TBO=540.
    DELTAT=TABS-TBO
    DELTAB=20.
C     CPW IS THE SPECIFIC HEAT OF THE SEA WATER,
C     BTU/LBM, TBO IS THE TEMPERATURE OF THE OUTPUT
```

```
C     BRINE FROM THE FLASH EVAPORATOR, DELTAT IS THE
C     TEMPERATURE DIFFERENCE ACROSS THE FLASH
C     EVAPORATOR, WH IS THE SEA WATER CIRCULATION,
C     LBM/HR, WD IS THE SEA WATER CIRCULATION,
C     GALLONS PER DAY, PR IS THE PERFORMANCE
C     RATIO, POUND OF DISTILLATE PRODUCED PER
C     1000 BTU OF HEAT REQUIRED
      WRITE(6,2) DELTAT
    2 FORMAT('0','THE TEMPERATURE DIFFERENCE ACROSS
     1THE DISTILLATION UNIT IS',F10.3)
      QREJ=QLOSS + QCOOL
      WH=QREJ/(CPW*DELTAB)
      WD=(QREJ/(CPW*(DELTAB)))*((7.48052*24)/64)
      WRITE(6,3) WH,WD
    3 FORMAT('0','THE REQUIRED SEA WATER CIRCULATION
     1IS',F15.3,'LBM/HR',10X,F15.3,'GALLONS PER DAY'
     2)
      M=(QREJ/LAMDAM)*(((DELTAT + 20)/DELTAB) - 1)
      WRITE(6,4) M
    4 FORMAT('0','THE FRESH WATER PRODUCED IS',
     1F15.3,' GALLONS PER DAY')
      PR=((M*64)/(7.48052*24))/(QREJ/1000)
      WRITE(6,6) PR
    6 FORMAT('0','THE PERFORMANCE RATIO IS',F10.6)
      K=K + 5
      A(JJ,1)=TOUT
      A(JJ,KK)=CETA
      A(JJ,KK + 1)=BETA
      B(JJ,1)=TOUT
      B(JJ,LL)=M
    5 CONTINUE
    1 CONTINUE
```

```
NN=2*N + 1
CALL PLOT(001,A,10,NN,0,1)
CALL PLOT(002,B,10,LL,0,1)
STOP
END
```

The program is set up to run on an IBM 370 computer. The program includes a plot routine which plots a graph of the cycle and Carnot efficiencies versus the turbine outlet temperature and a graph of the fresh water produced versus the turbine outlet temperature. The variable names are explained in the program.

FOOTNOTES

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